

**THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Appellant(s): Wang, et al.
Appl. No.: 10/506,418
Conf. No.: 8357
Filed: March 30, 2005
Title: BIODEGRADABLE MATERIALS FROM STARCH-GRAFTED POLYMERS
Art Unit: 1796
Examiner: O. Asinovsky
Docket No.: 117682-11

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

APPELLANTS' APPEAL BRIEF

Sir:

Appellants submit this Appeal Brief in support of the Notice of Appeal filed on June 2, 2008. This Appeal is taken from the Final Rejection in the Office Action dated March 18, 2008.

I. REAL PARTY IN INTEREST

The real party in interest for the above-identified patent application on Appeal is Cereplast, Inc. by virtue of an Assignment recorded on January 13, 2008 at reel 020436, frames 0968-0978 in the United States Patent and Trademark Office.

II. RELATED APPEALS AND INTERFERENCES

Appellant's legal representative and the Assignees of this patent application do not know of any prior or pending appeals, interferences or judicial proceedings that may be related to, directly affect or be directly affected by or have a bearing on the Board's decision with respect to the above-identified Appeal.

III. STATUS OF CLAIMS

Claims 1 and 3-18 are pending in this application. Claim 3 was previously canceled. Claim 19 was previously withdrawn. Claims 1 and 3-18 stand rejected. Therefore, Claims 1 and 3-18 are being appealed in this Brief. A copy of the appealed claims is included in the Claims Appendix.

IV. STATUS OF AMENDMENTS

A final Office Action was mailed on March 18, 2008. In the final Office Action, the Patent Office rejected Claims 1 and 3-18 as obvious in view of several references. Appellants filed a response to the final Office Action on May 14, 2008 with no amendments to the claims. An Advisory Action was mailed on May 21, 2008 maintaining the previous obviousness rejections. Appellants filed a Notice of Appeal on June 2, 2008 with respect to the obviousness rejections. A copy of the final Office Action and Advisory Action are attached as Exhibits A and B, respectively, in the Evidence Appendix.

V. SUMMARY OF CLAIMED SUBJECT MATTER

A summary of the claimed subject matter by way of reference to the specification and/or figures for each of the independent claims is provided as follows:

Independent Claim 1 is directed to a synthetic polymer and starch blend comprising 1-30 wt.% a granular and unplasticized starch (page 4, lines 12-13; page 5, lines 1-6 and 19-22; page 11, lines 1-14; page 21, lines 1-4) having a moisture content of less than about 1 (page 14, lines 12-13; page 16, lines 12-13); 1-24 wt.% a compatibilizer comprising a polymer and a grafting compound (page 4, lines 6-12; page 5, lines 7-18; page 8, lines 5-12; page 13, lines 3-17; page 21, lines 1-4), wherein the grafting compound is covalently bound to the polymer (page 9, lines 4-5; page 21, lines 13-14), and the remainder a second polymer (page 21, lines 1-4).

Independent Claim 10 is directed to a method for synthesizing a synthetic polymer and starch blend comprising mixing 1-30 wt.% granular and unplasticized starch (page 5, lines 1-6 and 19-22; page 11, lines 1-14; page 22, lines 8-10) having a moisture content of less than about 1% (page 14, lines 12-13; page 16, lines 12-13) with 1-24 wt.% compatibilizer comprising a polymer and a grafting compound (page 5, lines 7-18; page 8, lines 5-12; page 10, lines 1-6; page 13, lines 3-17), wherein the grafting compound is covalently bound to the polymer (page 9, lines 4-5; page 21, lines 13-14), and the remainder a second polymer (page 22, lines 8-10); and reacting the mixture such that the compatibilizer and the granular starch become covalently bound (page 4, lines 18-23; page 8, lines 5-12).

Independent Claim 17 is directed to a synthetic polyethylene and starch covalently bound mixture comprising 5-30 wt.% of a granular and unplasticized starch (page 5, lines 1-6 and 19-22; page 11, lines 1-14) selected from the group consisting of wheat starch, cornstarch, rice starch, potato starch or high amylose starch (page 10, lines 1-6), wherein the starch is not gelatinized and has a moisture content of less than about 1% (page 14, lines 12-13; page 16, lines 12-13; page 23, lines 16-17); a first polymer selected from the group consisting of polyethylene, polypropylene or polyethylene derivatives (page 8, lines 15-17; page 10, lines 11-17); a compatibilizer comprising a polymer and a grafting compound (page 5, lines 7-18; page 8, lines 5-12), the grafting compound being selected from the group consisting of maleic anhydride or chemicals having similar reactive properties (page 9, lines 2-10; page 11, lines 23-24; page 13, lines 3-17), and the polymer being covalently bound to the grafting compound (page 9, lines 4-

5; page 21, lines 13-14); wherein application of heat and pressure to the mixture produces covalent bonds between the compatibilizer and the starch (page 4, lines 18-23); wherein the compatibilizer is covalently bound to the first polymer (page 9, lines 4-5; page 21, lines 13-14); wherein the starch granules are 10-100 micrometers in diameter (page 24 line 1); wherein the compatibilizer is attached to approximately 5% of individual monomer units (page 5, lines 19-20); wherein the resulting mixture has similar mechanical properties to pure polyethylene (page 4, lines 1-2); and wherein the mixture absorbs relatively little water (page 5, lines 1-5).

Although specification citations are given in accordance with 37 C.F.R. §1.192(c), these reference numerals and citations are merely examples of support in the specification for the terms used in this section of the Brief. There is no intention to suggest in any way that the terms of the claims are limited to the examples in the specification. As demonstrated by the references numerals and citations, the claims are fully supported by the specification as required by law. However, it is improper under the law to read limitations from the specification into the claims. Pointing out specification support for the claim terminology in accordance with Rule 1.192(c) does not in any way limit the scope of the claims to those examples from which they find support. Nor does this exercise provide a mechanism for circumventing the law precluding reading limitations into the claims from the specification. In short, the references numerals and specification citations are not to be construed as claim limitations or in any way used to limit the scope of the claims.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. Claims 1 and 3-18 are rejected under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 5,115,000 to Jane et al. ("*Jane*") in view of U.S. Patent No. 5,510,401 to Dehennau et al. ("*Dehennau*") and in further view of U.S. Patent No. 6,242,503 to Kozma et al. ("*Kozma*"). Copies of *Jane*, *Dehennau* and *Kozma* are attached hereto as Exhibits C, D and E, respectively, in the Evidence Appendix.
2. Claims 1 and 3-17 are rejected under 35 U.S.C. §103(a) as being unpatentable over *Dehennau* in view of U.S. Patent No. 6,231,970 to Andersen et al. ("*Andersen*") and in view of *Kozma* and further in view of U.S. Patent No. 5,496,895 to Chinnaswamy et al. ("*Chinnaswamy*"). Copies of *Andersen* and *Chinnaswamy* are attached hereto as Exhibits F and G, respectively, in the Evidence Appendix.
3. Claim 18 is rejected under 35 U.S.C. §103(a) as being unpatentable over *Dehennau* in view of *Andersen* and in view of *Kozma* and further in view of *Chinnaswamy* and U.S. Patent No. 5,216,075 to Papazoglou et al. ("*Papazoglou*"). A copy of *Papazoglou* is attached hereto as Exhibit H in the Evidence Appendix.

VII. ARGUMENT

A. LEGAL STANDARDS

Obviousness under 35 U.S.C. §103

The Federal Circuit has held that the legal basis for a determination of obviousness under 35 U.S.C. § 103 is:

whether the claimed invention as a whole would have been obvious to a person of ordinary skill in the art at the time the invention was made...The foundational facts for the *prima facie* case of obviousness are: (1) the scope and content of the prior art; (2) the difference between the prior art and the claimed invention; and (3) the level of ordinary skill in the art...Moreover, objective indicia such as commercial success and long felt need are relevant to the determination of obviousness...Thus, each obviousness determination rests on its own facts.

In re Mayne, 41 U.S.P.Q. 2d 1451, 1453 (Fed. Cir. 1997).

In making this determination, the Patent Office has the initial burden of proving a *prima facie* case of obviousness. *In re Rijckaert*, 9 F.3d 1531, 1532, 28 U.S.P.Q. 2d 1955, 1956 (Fed. Cir. 1993). This burden may only be overcome “by showing some objective teaching in the prior art or that knowledge generally available to one of ordinary skill in the art would lead that individual to combine the relevant teachings.” *In re Fine*, 837 F.2d 1071, 1074, 5 U.S.P.Q. 2d 1596, 1598 (Fed. Cir. 1988). “If the examination at the initial stage does not produce a *prima facie* case of unpatentability, then without more the applicant is entitled to grant of the patent.” *In re Oetiker*, 24 U.S.P.Q. 2d 1443, 1444 (Fed. Cir. 1992).

Moreover, the Patent Office must provide explicit reasons why the claimed invention is obvious in view of the prior art. The Supreme Court has emphasized that when formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed. *KSR v. Teleflex*, 127 S. Ct. 1727 (2007).

Of course, references must be considered as a whole and those portions teaching against or away from the claimed invention must be considered. *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve Inc.*, 796 F.2d 443 (Fed. Cir. 1986). “A prior art reference may be considered

to teach away when a person of ordinary skill, upon reading the reference would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the Applicant.” *Monarch Knitting Mach. Corp. v. Fukuhara Indus. Trading Co., Ltd.*, 139 F.3d 1009 (Fed. Cir. 1998) (quoting *In re Gurley*, 27 F.3d 551 (Fed. Cir. 1994)).

B. THE CLAIMED INVENTION

There are three independent claims on appeal: Claims 1, 10 and 17. Independent Claim 1 is generally directed to a synthetic polymer and starch blend comprising a) 1-30 wt.% of a granular and unplasticized starch having a moisture content of less than about 1 and b) 1-24 wt.% of a compatibilizer comprising a polymer and a grafting compound. The grafting compound is covalently bound to the polymer. The remainder of the blend is a second polymer.

Independent Claim 10 is generally directed to a method for synthesizing a synthetic polymer and starch blend comprising mixing a) 1-30 wt.% of a granular and unplasticized starch having a moisture content of less than about 1% with b) 1-24 wt.% of a compatibilizer comprising a polymer and a grafting compound. The grafting compound is covalently bound to the polymer, and the remainder is a second polymer. The method further comprises reacting the mixture such that the compatibilizer and the granular starch become covalently bound.

Independent Claim 17 is generally directed to a synthetic polyethylene and starch covalently bound mixture comprising a) 5-30 wt.% of a granular and unplasticized starch selected from the group consisting of wheat starch, cornstarch, rice starch, potato starch or high amylose starch. The starch is not gelatinized and has a moisture content of less than about 1%. The mixture further comprises b) a first polymer selected from the group consisting of polyethylene, polypropylene or polyethylene derivatives and c) a compatibilizer comprising a polymer and a grafting compound. The grafting compound is selected from the group consisting of maleic anhydride or chemicals having similar reactive properties, and the polymer is covalently bound to the grafting compound. Application of heat and pressure to the mixture produces covalent bonds between the compatibilizer and the starch. The compatibilizer is covalently bound to the first polymer. The starch granules are 10-100 micrometers in diameter.

The compatibilizer is attached to approximately 5% of individual monomer units. The resulting mixture has similar mechanical properties to pure polyethylene, and the mixture absorbs relatively little water.

C. THE REJECTION OF CLAIMS 1 AND 3-18 UNDER 35 U.S.C. §103(A) TO JANE, DEHENNAU AND KOZMA SHOULD BE REVERSED BECAUSE THE EXAMINER HAS FAILED TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNESS WITH RESPECT TO CLAIMS 1 AND 3-18

Independent Claims 1, 10 and 17 recite, in part, a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch having a moisture content of less than about 1%. As discussed in more detail below, the advantages of the claimed invention rely, in part, on using a starch that is unplasticized and has a moisture content of less than about 1%. In contrast, Appellants respectfully submit that, even if combined, the cited references fail to disclose or suggest every element of independent Claims 1, 10 and 17.

Conventional mixtures of starch and polymers have resulted in materials with poor physical qualities. Starch generally does not mix well with typical polymers such as polyethylene, polypropylene, etc. In an attempt to improve these mixtures, some researchers have used high amylose starch. Although high amylose starch slightly improves the physical properties of the mixtures, it is relatively expensive and reduces or eliminates the cost benefits of these mixtures. Gelatinized starch has also been used in an attempt to improve these mixtures. However, gelatinized starch as well as high amylose starch requires the addition of a plasticizer.

In existing starch/polymer blends, a plasticizer is utilized to facilitate blending of the starch and polymer. The addition of a plasticizer poses several disadvantages. First, it requires processing of the starch, which increases the cost. In addition, plasticizers such as glycerol increase the water absorbency of the polymer and starch mixture. This has a deleterious effect on the mixture's physical properties, making them impractical to use.

An advantage of the claimed synthetic polymer and starch blend is that the starch is unplasticized (e.g. lacks a plasticizer) and has a moisture content of less than about 1%. By eliminating the need for a plasticizer, for example, by replacing it with a compatibilizer in accordance with the claimed blend, the water absorbency of the final polymer and starch blend

can be reduced. Moreover, the low moisture content of the starch ensures that very little moisture is in the polymer and starch blend to begin with. The absence of the plasticizer and the low moisture content of the starch provides for a stronger, more durable product made from the polymer/starch blend. See specification, Examples 1 and 2.

Jane fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch having a moisture content of less than about 1% as required by independent Claims 1, 10 and 17. *Jane* is directed to starch plastics that incorporate modified polyethylene. At no point does *Jane* teach using a starch that has a moisture content of less than about 1% or drying a starch to give a moisture content of less than about 1%. The Examiner admits same. See Office Action dated March 18, 2008, page 4.

The Examiner alleges that *Jane* must “inherently” disclose a starch having a moisture content of less than about 1% because *Jane* teaches heating the components of his starch-based product at 110 °C to 200 °C while blending. Appellants respectfully disagree with the Examiner’s inherency argument that *Jane* inherently discloses a starch having a moisture content of less than about 1% based solely on the blended components being heated.

As shown in Chapter 4 of the publication Technology of Corn Wet Milling and Associated Process by Paul Harwood Blanchard, 2002 (attached as Exhibit I), starch typically has a moisture content of 12%. See *id.* at 141-142. It takes a great deal of time and energy to reduce the moisture content of starch to less than about 1%. For example, as described in Examples 1-2, Appellants dried cornstarch at 120 °C for 24 hours to reach a moisture content of less than 1% prior to the sample preparation. Moreover, the cornstarch was dried at 120 °C for 24 hours prior to blending the cornstarch with any other components, which would have reduced the drying efficiency of the starch.

Jane teaches heating the starch of his starch-based product at 110 °C to 200 °C as it is blended with the oxidized polyethylene and unmodified polyethylene. *Jane* does not teach using the high temperature blending to remove moisture from the starch or even suggest the need for reducing the moisture content of the starch to below 1% as a starting material as a way to improve the quality of his product. Even at processing temperatures of at 110 °C to 200 °C, blending the starch with other components is likely to prevent substantial moisture from being removed from the starch unless the blending was done for an extremely long time. However, *Jane* does require any specific time or duration for blending the starch-based product at this

temperature. In fact, *Jane* teaches that the time for heating and blending to occur is not critical to the process. See *Jane*, column 4, lines 22-23. As a result, *Jane* is not interested in reducing the moisture content of the starch to less than about 1% or utilizing this reduced moisture starch in accordance with the present claims.

Moreover, *Jane* even teaches a very short mixing time. In one example, *Jane* teaches that for a screw extruder, one calculates the mixing time by determining the length of the barrel and dividing this by the number of flights to obtain the pitch. See *Jane*, column 4, lines 25-35. The revolutions per minute are multiplied by the pitch to obtain the screw speed. The length of the barrel is divided by the screw speed to obtain the mixing time. In the example, the barrel length was 31.24 inches, and there were 25 flights yielding a pitch of 1.25 inches. At 15 rpm, the screw speed is 18.75 inches per minute. The mixing time is then calculated at 1.67 minutes. At a mixing time of 1.67 minutes for the blend, it is highly unlikely that the starch (initial moisture content of ~12%) will have its moisture reduced below 1% even in the absence of being blended with other components.

To satisfy the test for inherency, heating the components of *Jane's* starch-based product at 110 °C to 200 °C to evaporate water from the product would necessarily (i.e. always or automatically) reduce the moisture content of the starch to less than about 1%. That condition simply is not met under the present circumstances as previously discussed. The fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic. See, MPEP 2112. *In re Rijckaert*, 9 F.3d 1531, 1534, 28 USPQ2d 1955, 1957 (Fed. Cir. 1993) (reversed rejection because inherency was based on what would result due to optimization of conditions, not what was necessarily present in the prior art). Consequently, the Examiner has failed to provide a basis in fact or technical reasoning to support the determination that the allegedly inherent characteristic of a starch having a moisture content of less than about 1% necessarily flows from the teachings of *Jane*.

Dehennau fails to remedy the deficiencies of *Jane*. For example, *Dehennau* fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch as required by independent Claims 1, 10 and 17. *Dehennau* is directed to an alloy composition that possesses improved properties of transparency and mechanical resistance. The alloy composition comprises a starch and a polymer acting as coupling agent comprising polyolefins modified by chemical functional groups that are active towards the

hydroxyl functional groups of starch. *Dehennau* specifically teaches that the use of starch supplemented with a plasticizer, in particular glycerine, diglycerine, polyglycerine and/or sorbitol, can prove to be advantageous in many cases. See *Dehennau*, column 3, lines 11-13. As a result, *Dehennau* not only fails to disclose or suggest a 1-30 wt.% of an unplasticized starch, *Dehennau* teaches away from same.

Dehennau also fails to disclose or suggest an unplasticized starch having a moisture content below 1%. Instead, *Dehennau* teaches using a starch that retains its initial moisture (~12%) or has water added to it, which teaches away from the present claims. *Dehennau* discloses in Examples 13 and 14 that a normal, native and non-dried maize starch (12.5% by weight of water) is mixed with glycerine and another polymer and processed together to produce his film. *Dehennau* further teaches that starches used are of natural and plant origin and may be structurally modified, pregelatinised or modified after the addition of water and/or a plasticizer. See *Dehennau*, column 3, lines 17-23.

Kozma fails to remedy the deficiencies of *Dehennau*. For example, *Kozma* fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch as required by independent Claims 1, 10 and 17. *Kozma* also fails to disclose or suggest an unplasticized starch having a moisture content of less than about 1% as required by independent Claims 1, 10 and 17. In fact, *Kozma* fails to even disclose or suggest the use of any starch in his polymer articles.

For at least the reasons identified above, even if combined, *Jane*, *Dehennau* and *Kozma* fail to disclose or even suggest every element of independent Claims 1, 10 and 17, as well as Claims 3-9, 11-16 and 18 that depend from Claims 1, 10 and 17. Moreover, the cited references fail to even recognize the advantages, benefits and/or properties of a synthetic polymer and starch blend made in accordance with Claims 1, 10 and 17. Accordingly, Appellants respectfully submit that Claims 1 and 3-18 are novel, nonobvious and distinguishable from the cited references and are in condition for allowance.

D. THE REJECTION OF CLAIMS 1 AND 3-17 UNDER 35 U.S.C. §103(A) TO DEHENNAU, ANDERSEN, KOZMA AND CHINNASWAMY SHOULD BE REVERSED BECAUSE THE EXAMINER HAS FAILED TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNESS WITH RESPECT TO CLAIMS 1 AND 3-17

Independent Claims 1, 10 and 17 recite, in part, a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch having a moisture content of less than about 1%. As previously discussed, an advantage of the claimed synthetic polymer and starch blend is that the starch is unplasticized (e.g. lacks a plasticizer) and has a moisture content of less than about 1%. In contrast, Appellants respectfully submit that, even if combined, *Dehennau*, *Andersen*, *Kozma* and *Chinnaswamy* fail to disclose or suggest every element of independent Claims 1, 10 and 17.

Dehennau fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch as required by independent Claims 1, 10 and 17 and actually teaches away from same. *Dehennau* is directed to an alloy composition comprising a starch and a polymer acting as coupling agent comprising polyolefins modified by chemical functional groups. *Dehennau* specifically teaches the advantages of using starch supplemented with a plasticizer, in particular glycerine, diglycerine, polyglycerine and/or sorbitol, to produce the alloy composition. See *Dehennau*, column 3, lines 11-13. As a result, *Dehennau* fails to disclose and teaches away from a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch in accordance with the present claims.

Dehennau also fails to disclose or suggest an unplasticized starch having a moisture content below 1% and teaches away from same. For example, *Dehennau* teaches using a starch that retains its initial moisture (~12%) or has water added to it. *Dehennau* discloses in Examples 13 and 14 that a normal, native and non-dried maize starch (12.5% by weight of water) is mixed with glycerine and another polymer and processed together to produce his film. *Dehennau* further teaches that starches used are of natural and plant origin and may be structurally modified, pregelatinised or modified after the addition of water and/or a plasticizer. See *Dehennau*, column 3, lines 17-23.

Kozma fails to remedy the deficiencies of *Dehennau*. *Kozma* fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch as required by independent Claims 1, 10 and 17. *Kozma* also fails to disclose or suggest an

unplasticized starch having a moisture content of less than about 1% as required by independent Claims 1, 10 and 17. In fact, *Kozma* fails to even disclose or suggest the use of any starch in his polymer articles.

Andersen fails to remedy the deficiencies of *Dehennau*. *Andersen* fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch as required by independent Claims 1, 10 and 17. *Andersen* is directed to thermoplastic starch compositions having a particulate filler. *Andersen* specifically teaches that the starch compositions include two or more chemically or physically distinct materials or phases such as the binding matrix comprising, at a minimum, a starch melt formed by plasticizing starch with a plasticizer, a particulate filler and optional admixtures. See *Andersen*, column 11, lines 35-40. *Andersen* further teaches that these materials impart one or more unique properties to the final thermoplastic starch compositions made therefrom, as well as to the sheets, films and other articles manufactured therefrom. See *Andersen*, column 11, lines 43-46. As a result, *Andersen* requires the use of plasticized starch to form the starch melt, which not only fails to disclose the present claims but actually teaches away from same.

Chinnaswamy fails to remedy the deficiencies of *Dehennau*. *Chinnaswamy* fails to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch as required by independent Claims 1, 10 and 17. *Chinnaswamy* also fails to disclose or suggest an unplasticized starch having a moisture content of less than about 1% as required by independent Claims 1, 10 and 17. *Chinnaswamy* is directed to biodegradable plastic made by mixing starches and a non-biodegradable polymer such as a polystyrene, polyurethane, polyethylene, polypropylene, or polycarbonate and, in the presence of an added oxidizing agent, treating the mixture under heat, pressure and reagents to break the polymers. Nevertheless, *Chinnaswamy* fails to disclose or suggest using any unplasticized starch that has a moisture content of less than about 1% or even drying an unplasticized starch to give a moisture content of less than about 1%.

For at least the reasons identified above, even if combined, *Dehennau*, *Andersen*, *Kozma* and *Chinnaswamy* fail to disclose or even suggest every element of independent Claims 1, 10 and 17, as well as Claims 3-9, 11-16 and 18 that depend from Claims 1, 10 and 17. Moreover, the cited references fail to even recognize the advantages, benefits and/or properties of a synthetic polymer and starch blend made in accordance with Claims 1, 10 and 17. Accordingly,

Appellants respectfully submit that Claims 1 and 3-18 are novel, nonobvious and distinguishable from the cited references and are in condition for allowance.

E. THE REJECTION OF CLAIM 18 UNDER 35 U.S.C. §103(A) TO *DEHENNAU, ANDERSEN, KOZMA, CHINNASWAMY* AND *PAPAZOGLU* IS IMPROPER IN VIEW OF THE PATENTABILITY OF INDEPENDENT CLAIM 1

Claim 18 stands rejected under 35 U.S.C. §103(a) as being unpatentable over *Dehennau, Andersen, Kozma, Chinnaswamy* and *Papazoglou*. Appellants respectfully submit that the patentability of Claim 1 over *Dehennau, Andersen, Kozma* and *Chinnaswamy* as discussed above also demonstrates that the obviousness rejection of Claim 18, which depends from Claim 1, is improper. In this regard, even with *Papazoglou* as a reference, the cited art fails to teach or suggest the elements of Claim 18 in combination with the novel elements of Claim 1.

For example, even if combined, *Dehennau, Andersen, Kozma*, and *Chinnaswamy* fail to disclose or suggest a synthetic polymer and starch blend comprising 1-30 wt.% of an unplasticized starch or an unplasticized starch having a moisture content of less than about 1% as required by independent Claims 1, 10 and 17. *Papazoglou* fails to remedy the deficiencies of *Dehennau, Andersen, Kozma*, and *Chinnaswamy*. *Papazoglou* is directed to moldable multi-phase polyblends comprising blends of a polyamide, a thermoplastic copolymer of an α,β -unsaturated carboxylic acid and a monovinyl aromatic monomer, and an anhydride-functionalized elastomer. *Papazoglou* fails to even disclose or suggest the use of any starch, whether plasticized or not, in his polymer articles.

Accordingly, Appellants respectfully submit that Claim 18 that depends from Claim 1 is novel, nonobvious and distinguishable from the cited references and is in condition for allowance.

VIII. CONCLUSION

Appellants respectfully submit that the Examiner has failed to establish a *prima facie* case of obviousness under 35 U.S.C. §103 with respect to the rejections of Claims 1 and 3-18. Accordingly, Appellants respectfully submit that the obviousness rejections are erroneous in law and in fact and should therefore be reversed by this Board.

A check in the amount of \$510 is submitted herewith to cover the cost of the Appeal Brief. The Director is authorized to charge any additional fees that may be required, or to credit any overpayment to Deposit Account No. 02-1818. If such a withdrawal is made, please indicate the Attorney Docket No. 117682-11 on the account statement.

Respectfully submitted,

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Dated: July 29, 2008

CLAIMS APPENDIX

PENDING CLAIMS ON APPEAL OF U.S. PATENT APPLICATION SERIAL NO. 10/506,418

1. A synthetic polymer and starch blend comprising:
1-30 wt.% a granular and unplasticized starch having a moisture content of less than about 1%;
1-24 wt.% a compatibilizer comprising a polymer and a grafting compound, wherein said grafting compound is covalently bound to said polymer, and
the remainder a second polymer.
3. The blend of Claim 1 wherein said starch is selected from the group consisting of cornstarch, wheat starch, rice starch, and potato starch.
4. The blend of Claim 1 wherein said compatibilizer is comprised of 75-98 wt.% polymer and 2-25 wt.% grafting compound.
5. The blend of Claim 4 wherein said grafting compound is maleic anhydride.
6. The blend of Claim 4 wherein the polymer of the compatibilizer is selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-styrene), poly(ethylene terephthalate), polyvinyl fluoride, polyvinyl chloride, or derivatives thereof.

7. The blend of claim 4 wherein said grafting compound comprises 5 wt.% of said compatibilizer.
8. The blend of claim 1 wherein said second polymer is selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-styrene), poly(ethylene terephthalate), polyvinyl fluoride, polyvinyl chloride, or derivatives thereof.
9. The blend of Claim 1 wherein said second polymer is polyethylene.
10. A method for synthesizing a synthetic polymer and starch blend, comprising:
mixing 1-30 wt.% granular and unplasticized starch having a moisture content of less than about 1% with 1-24 wt.% compatibilizer comprising a polymer and a grafting compound, wherein said grafting compound is covalently bound to said polymer, and the remainder a second polymer; and
reacting the mixture such that the compatibilizer and the granular starch become covalently bound.
11. The method of Claim 10 wherein said reacting comprises applying heat and pressure.
12. The method of Claim 10 wherein said compatibilizer comprises 1-20 wt.% grafting compound and 80-99 wt.% polymer.

13. The method of Claim 12 wherein said grafting compound is maleic anhydride.
14. The method of Claim 12 wherein said grafting compound comprises 5 wt.% of said compatibilizer.
15. The method of Claim 12 wherein the polymer of the compatibilizer is selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-styrene), poly(ethylene terephthalate), polyvinyl fluoride, polyvinylchloride, or derivatives thereof.
16. The method of Claim 10 wherein said second polymer is selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-styrene), poly(ethylene terephthalate), polyvinyl fluorides, polyvinyl chloride, or derivatives thereof.

17. A synthetic polyethylene and starch covalently bound mixture comprising:

5-30 wt.% of a granular and unplasticized starch selected from the group consisting of wheat starch, cornstarch, rice starch, potato starch or high amylose starch, wherein said starch is not gelatinized and has a moisture content of less than about 1%;

a first polymer selected from the group consisting of polyethylene, polypropylene or polyethylene derivatives;

a compatibilizer comprising a polymer and a grafting compound, the grafting compound being selected from the group consisting of maleic anhydride or chemicals having similar reactive properties, and the polymer being covalently bound to the grafting compound;

wherein application of heat and pressure to the mixture produces covalent bonds between the compatibilizer and the starch;

wherein said compatibilizer is covalently bound to said first polymer;

wherein said starch granules are 10-100 micrometers in diameter;

wherein said compatibilizer is attached to approximately 5% of individual monomer units;

wherein the resulting mixture has similar mechanical properties to pure polyethylene; and

wherein said mixture absorbs relatively little water.

18. The synthetic polymer and starch blend of Claim 1 wherein the second polymer is selected from the group consisting of polyethylene, polypropylene, polystyrene, polybutylene, poly(styrene-ethylene-butylene-styrene), poly(ethylene terephthalate), polyvinyl fluoride, polyvinyl chloride or derivatives thereof and the compatibilizer is comprised of maleic anhydride grafted poly(styrene-ethylene-butylene-styrene).

EVIDENCE APPENDIX

- EXHIBIT A: Final Office Action dated March 18, 2008
- EXHIBIT B: Advisory Action dated May 21, 2008
- EXHIBIT C: U.S. Patent No. 5,115,000 to Jane et al. ("*Jane*"), cited by the Examiner in the Office Action dated March 18, 2008
- EXHIBIT D: U.S. Patent No. 5,510,401 to Dehennau et al. ("*Dehennau*"), cited by the Examiner in the Office Action dated March 18, 2008
- EXHIBIT E: U.S. Patent No. 6,242,503 to Kozma et al. ("*Kozma*"), cited by the Examiner in the Office Action dated March 18, 2008
- EXHIBIT F: U.S. Patent No. 6,231,970 to Andersen et al. ("*Andersen*"), cited by the Examiner in the Office Action dated March 18, 2008
- EXHIBIT G: U.S. Patent No. 5,496,895 to Chinnaswamy et al. ("*Chinnaswamy*"), cited by the Examiner in the Office Action dated March 18, 2008
- EXHIBIT H: U.S. Patent No. 5,216,075 to Papazoglou et al. ("*Papazoglou*"), cited by the Examiner in the Office Action dated March 18, 2008
- EXHIBIT I: Chapter 4 of the publication Technology of Corn Wet Milling and Associated Process

RELATED PROCEEDINGS APPENDIX

None

EXHIBIT A



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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10/506,418

03/30/2005

Ya-Jane Wang

117682-011

8357

24573 7590 03/18/2008
BELL, BOYD & LLOYD, LLP
P.O. Box 1135
CHICAGO, IL 60690

References Downloaded

EXAMINER

ASINOVSKY, OLGA

ART UNIT	PAPER NUMBER
----------	--------------

1796

MAIL DATE	DELIVERY MODE
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03/18/2008

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

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117682-011

011

Office Action Summary	Application No.	Applicant(s)	
	10/506,418	WANG ET AL.	
	Examiner	Art Unit	
	OLGA ASINOVSKY	1796	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 02 January 2008.
- 2a) ☒ This action is **FINAL**. 2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1 and 3-19 is/are pending in the application.
- 4a) Of the above claim(s) 19 is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1 and 3-19 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☒ The drawing(s) filed on 30 March 2005 is/are: a) ☒ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. _____.
 3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|----------------------------------------------------------------------------------------|-------------------------------------------------------------------|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413) |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | Paper No(s)/Mail Date. _____ |
| 3) <input checked="" type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08) | 5) <input type="checkbox"/> Notice of Informal Patent Application |
| Paper No(s)/Mail Date <u>01/02/2008</u> . | 6) <input type="checkbox"/> Other: _____ |

DETAILED ACTION

Response to Amendment

1. Applicants amend each independent claim 1, 10 and 17 by the definition that a granular starch is unplasticized and has a moisture content of less than about 1%, and a compatibilizer comprises a polymer and a grafting compound, wherein said grafting compound is covalently bound to the polymer. The term "unplasticized" is supported in the original specification at page 11, line. The "moisture content of less than about 1%" is supported at page 14 in the example 1.

2. Cancellation of claim 2 is noted

3. Upon the present amendment, the reconsideration of the rejections over the cited references in the mailed office action of 11/29/2007 is made in the present office action below.

4. Newly submitted claim 19 is directed to an invention that is independent or distinct from the invention originally claimed for the following reasons: new claim 19 is depending on claim 1. New claim 19 drawn to a compatibilizer comprising a polymer and a grafting compound, wherein said grafting compound is covalently bound to a polymer, wherein the grafting compound is selected from the group consisting of epoxides. Although a compatibilizer in claim 1 is generic, the compatibilizer is a maleic anhydride (original claims 5 and 13), or maleic anhydride cited under Markush group practice in the independent claim 17, and focusing on preferred maleic anhydride in the working example in the original specification. In claim 19 wherein the grafting compound

is covalently bound to a polymer, wherein the grafting compound is selected from the group consisting of epoxides will require a new search.

Since applicant has received an action on the merits for the originally presented invention, this invention has been constructively elected by original presentation for prosecution on the merits. Accordingly, claim 19 is withdrawn from consideration as being directed to a non-elected invention. See 37 CFR 1.142(b) and MPEP § 821.03.

Claim Rejections - 35 USC § 103

5. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 1 and 3-18 are rejected under 35 U.S.C. 103(a) as being unpatentable over Jane et al U.S. Patent 5,115,000 in view of Dehennau et al U.S. Patent 5,510,401 and further in view of Kozma et al U.S. Patent 6,242,503 as evidence for forming a covalent bond between the polymer and the maleic anhydride.

All references have been considered in the previous office action mailed on 11/29/2007. Jane discloses a composition comprising a granular starch, oxidized polyethylene and polyethylene which has not been modified, column 2, lines 4-7 and 27. Granular starch includes unmodified starches, col. 2, line 12. The unmodified starch is readable in the present claims 1, 3-18. The starch comprises up to 50% of the composition. The oxidized polyethylene comprises up to 15% of the composition, and the remaining

amount is the polyethylene, column 1, lines 59-66. The amount of the ingredients is readable in the present claims. The oxidized polyethylene is a compatibilizer agent between the starch and polyethylene, column 2, lines 32-37, for the present claims 1, 10 and 17. The carboxy groups on the oxidized polyethylene form ester bonds with the hydroxyl groups on the starch, column 2, lines 36-38. Jane discloses a process for synthesizing a biodegradable plastic composition. The components are blended while heated at a temperature of 110 C to 200 C, column 1, lines 61-62. Although, Jane does not mention about claimed moisture content of less than 1% of the granular starch, this statement is inherent, because upon the heating the components at 110 to 200 C water is evaporate.

Jane does not mention that a grafting compound is covalently attached to a polymer.

Dehennau discloses a biodegradable film produced from a composition comprising a starch, polyethylene modified by grafting maleic anhydride and a non-modified polyethylene, column 6, lines 20-35, for the present claims. The maleic anhydride grafted on to polyethylene is readable for being claimed compatibilizer in the present claims. The starch includes a wheat starch and/or potato starch, column 3, lines 27-28. The starch may be dried, column 4, line 7. The polymer serving as the coupling agents=compatibilizer are active towards the hydroxyl functional groups of the starch, column 3, lines 44-48. A process for producing a biodegradable film includes step of mixing the ingredients under 160 C, column 4, line 31.

Dehennau does not mention that maleic anhydride is covalently bound polyethylene.

Jane and Dehennau inventions belong to the analogous prior art similar utility for producing a biodegradable polymer.

Kozma discloses the maleated polyethylene, wherein maleic anhydride-grafting is covalently bonding one or more maleic anhydride groups to the original polymer chains, column 4, lines 23-29 and column 7, lines 35-37.

Kozma is cited an evidence for creating covalent bond between the polyethylene and grafted maleic anhydride.

It would have been obvious to one of ordinary skill in the art to substitute the carboxylic groups containing oxidized polyethylene in Jane invention with a grafted maleated anhydride modified polyethylene in Dehennau invention because oxidized polyethylene in Jane invention and maleated polyethylene in Dehennau belong to the analogous organic acid functionalized polyethylene, and such modification will not change the chemical reaction with starch component; and in light of the evidence in Kozma invention, the covalent bond between the polyethylene and grafted maleic anhydride is also created in Dehennau invention since the same polyethylene and the same grafted maleic anhydride are readable in Dehennau and Kozma invention in absence of any unexpected results.

6. Claims 1, 3-17 are rejected under 35 U.S.C. 103(a) as being unpatentable over Dehennau et al U.S. Patent 5,510,401 in view of Andersen et al U.S. Patent 6,231,970 and in view of Kozma et al U.S. Patent 6,242,503, and further in view of Chinnaswamy et al U.S. Patent 5,496,895.

Dehennau and Kozma have been considered above.

Dehennau does disclose starch, which can be dried; graft maleated polyethylene and polyethylene. Dehennau does not mention a low moisture content of dried starch.

Andersen discloses thermoplastic starch composition, wherein starch is in unmodified state in granular form and dried, column 2, lines 33-35 and 39, 52. Water can be removed before processing by using starch that has been predried, or alternatively, water can removed during processing the molten mixture, column 4, lines 32-35. The moisture content is below about 1%, column 20, lines 35-41.

In light of the dried condition of starch to the moisture content below to 1% as disclosed in Andersen invention, it would be obvious to one of ordinary skill in the art to substitute a dried starch in Dehennau invention with a dried starch having low moisture content in Andersen invention for the purposes to improve stability of starch during the starch/polymer melt process and eliminate gassing impurity.

Dehennau does not mention that a grafting compound=maleic anhydride is covalently attached to a polymer.

Kozma is cited as evidence for creating covalent bond between the polyethylene and grafted maleic anhydride.

It would have been obvious to one of ordinary skill in the art at the time of the invention to use known technique for creating covalent bond between the polyethylene and grafted maleic anhydride in Kozma invention for the analogous polyethylene grafted with maleic anhydride in Dehennau invention since the same results would be expected, and thereby obtain the claimed requirement wherein the maleic anhydride is covalently attached to the polyethylene.

Dehennau does not disclose that the compatibilizer and the granular starch become covalently bound in the present claim 10, wherein the compatibilizer comprises a grafting compound and polymer.

Chinnaswamy discloses biodegradable polymer composition comprising a starch and non-biodegradable plastic, wherein the non-biodegradable polymer is treated by adding an oxidizing agent. The non-biodegradable polymer includes any alkyne or alkene chain including polyethylene, polypropylene, polystyrene, column 3, lines 33-38, for the present claims 6 and 10. The oxidizing agent includes (met)acrylic acid, column 3, lines 46 and 54. The treatment (by adding an oxidizing agent under heat and pressure) creates reactive groups such as aldehyde or hydroxyl groups on the non-biodegradable polymers. The starch and the treated non-biodegradable plastic covalently bound to each other, claim 1 at column 8. The compatibilizer in claim 10 is maleic anhydride

Art Unit: 1796

grafted polymer referring to the present claims 12 and 13. Chinnaswamy does disclose that starch and the treated non-biodegradable polymer are covalently bound.

It would have been obvious to one of ordinary skill in the art at the time of the invention to use the known method for creating covalent bond between the maleic anhydride grafted polyethylene and starch in Chinnaswamy invention for the analogous process for producing a biodegradable film comprising polyethylene grafted with maleic anhydride and starch in Dehennau invention for obtaining the adequate results, and thereby, obtain the claimed requirement wherein the compatibilizer and the starch are covalently bound.

7. Claim 18 is rejected under 35 U.S.C. 103(a) as being unpatentable over Dehennau et al U.S. Patent 5,510,401 in view of Andersen et al U.S. Patent 6,231,970 and in view of Kozma et al U.S. Patent 6,242,503, and further in view of Chinnaswamy et al U.S. Patent 5,496,895 as applied to claims 1, 3-17 above, and further in view of Papazoglou U.S. patent 5,216,075.

Dehennau does not disclose the claimed compatibilizer that is maleic anhydride grafted poly(styrene-ethylene-butylene-styrene) in the present claim 18.

In light of the discussions in the paragraph 6 above, the unmodified dried starch granules can have low moisture content by teaching in Andersen invention. The grafted polymers having functional groups have chemical reaction with the hydroxyl functional groups of the starch.

Papazoglou discloses maleated block copolymer such as functionalized styrene-ethylene/1-butene-styrene (S-E/B-S) rubber, column 7, lines 43-50. The maleated (S-E/B-S) block copolymer is commercially available.

It would have been obvious to one of ordinary skill in the art to substitute the grafted maleic anhydride polyethylene in Dehennau invention with maleated block copolymer (S-E/B-S) in Papazoglou invention as potential options because maleated polypropylene in Dehennau and maleated block copolymer in Papazoglou work equally well to create a chemical reaction with starch with reasonable expectation of success.

The closest reference Patent 5,667,574 to Zhang cited under X category in the PCT/US03/05661 has been considered. While Zhang discloses unmodified starch, coupling agent and alpha-olefin polymer, Zhang does not disclose a covalent bond between the coupling agent and alpha-olefin polymer.

Conclusion

8. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not

mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to OLGA ASINOVSKY whose telephone number is (571)272-1066. The examiner can normally be reached on 9:00 to 5:30 pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Randy Gulakowski can be reached on 571-272-1302. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR.

Application/Control Number: 10/506,418
Art Unit: 1796

Page 11

Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Randy Gulakowski/
Supervisory Patent Examiner, Art Unit 1796

Olga Asinovsky
Examiner
Art Unit 1796

March 1, 2008

Notice of References Cited	Application/Control No. 10/506,418	Applicant(s)/Patent Under Reexamination WANG ET AL.	
	Examiner OLGA ASINOVSKY	Art Unit 1796	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,231,970	05-2001	Andersen et al.	428/332
	B	US-			
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number	10506418
Filing Date	2002-09-24
First Named Inventor	Wang, Ya-June
Art Unit	1711
Examiner Name	Olga Asinovsky
Attorney Docket Number	ARK007-157/02157A/SMD

U.S. PATENTS

Remove

Examiner Initial*	Cite No	Patent Number	Kind Code ¹	Issue Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
/OA/	1	5667574		1997-09-16	Zhang Yuan Qing	
/OA/	2	5415827		1995-05-16	Tomka et al.	
/OA/	3	5627223		1997-05-06	Dehennau et al.	
/OA/	4	5461094		1995-10-24	Yoo et al.	
/OA/	5	5115000		1992-05-19	Jane et al.	

If you wish to add additional U.S. Patent citation information please click the Add button.

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U.S. PATENT APPLICATION PUBLICATIONS

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Examiner Initial*	Cite No	Publication Number	Kind Code ¹	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
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**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**
(Not for submission under 37 CFR 1.99)

Application Number	10506418
Filing Date	2002-09-24
First Named Inventor	Wang, Ya-June
Art Unit	1711
Examiner Name	Olga Asinovsky
Attorney Docket Number	ARK007-157/02157A/SMD

Examiner Initial*	Cite No	Foreign Document Number ³	Country Code ² ;	Kind Code ⁴	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T ⁵
	1							<input type="checkbox"/>

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NON-PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T ⁵
IOA/	1	"Effects of Glycerol and PE-g-MA on Morphology, Thermal and Tensile Properties of LDPE and Rice Starch Blends", Y.J. Wang, W. Liu, Z. Sun, Journal of Applied Polymer Science, Vol 92, 344-350, 12 August 2003	<input type="checkbox"/>
IOA/	2	"Technology of Corn Wet Milling and Associated Processes," Blanchard, Paul Harwood, Industrial Chemistry Library, Vol 4, 127-154, 1992	<input type="checkbox"/>

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EXAMINER SIGNATURE

Examiner Signature	/Olga Asinovsky/ (02/29/2008)	Date Considered	
--------------------	-------------------------------	-----------------	--

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

¹ See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. ² Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). ³ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁴ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁵ Applicant is to place a check mark here if English language translation is attached.

EXHIBIT B



UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/506,418	03/30/2005	Ya-Jane Wang	117682-011	8357
24573 7590 05/21/2008 BELL, BOYD & LLOYD, LLP P.O. Box 1135 CHICAGO, IL 60690			EXAMINER ASINOVSKY, OLGA	
			ART UNIT 1796	PAPER NUMBER
			MAIL DATE 05/21/2008	DELIVERY MODE PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

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MAY 27 2008

ATTY: MB-nyB
DOCKET #: 117682-011

**Advisory Action
Before the Filing of an Appeal Brief**

Application No.

10/506,418

Applicant(s)

WANG ET AL.

Examiner

OLGA ASINOVSKY

Art Unit

1796

--The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

THE REPLY FILED 14 May 2008 FAILS TO PLACE THIS APPLICATION IN CONDITION FOR ALLOWANCE.

1. ☒ The reply was filed after a final rejection, but prior to or on the same day as filing a Notice of Appeal. To avoid abandonment of this application, applicant must timely file one of the following replies: (1) an amendment, affidavit, or other evidence, which places the application in condition for allowance; (2) a Notice of Appeal (with appeal fee) in compliance with 37 CFR 41.31; or (3) a Request for Continued Examination (RCE) in compliance with 37 CFR 1.114. The reply must be filed within one of the following time periods:

- a) ☒ The period for reply expires 3 months from the mailing date of the final rejection.
b) ☐ The period for reply expires on: (1) the mailing date of this Advisory Action, or (2) the date set forth in the final rejection, whichever is later. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of the final rejection.

Examiner Note: If box 1 is checked, check either box (a) or (b). ONLY CHECK BOX (b) WHEN THE FIRST REPLY WAS FILED WITHIN TWO MONTHS OF THE FINAL REJECTION. See MPEP 706.07(f).

Extensions of time may be obtained under 37 CFR 1.136(a). The date on which the petition under 37 CFR 1.136(a) and the appropriate extension fee have been filed is the date for purposes of determining the period of extension and the corresponding amount of the fee. The appropriate extension fee under 37 CFR 1.17(a) is calculated from: (1) the expiration date of the shortened statutory period for reply originally set in the final Office action; or (2) as set forth in (b) above, if checked. Any reply received by the Office later than three months after the mailing date of the final rejection, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

NOTICE OF APPEAL

2. ☐ The Notice of Appeal was filed on _____. A brief in compliance with 37 CFR 41.37 must be filed within two months of the date of filing the Notice of Appeal (37 CFR 41.37(a)), or any extension thereof (37 CFR 41.37(e)), to avoid dismissal of the appeal. Since a Notice of Appeal has been filed, any reply must be filed within the time period set forth in 37 CFR 41.37(a).

AMENDMENTS

3. ☐ The proposed amendment(s) filed after a final rejection, but prior to the date of filing a brief, will not be entered because
(a) ☐ They raise new issues that would require further consideration and/or search (see NOTE below);
(b) ☐ They raise the issue of new matter (see NOTE below);
(c) ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal; and/or
(d) ☐ They present additional claims without canceling a corresponding number of finally rejected claims.

NOTE: _____. (See 37 CFR 1.116 and 41.33(a)).

4. ☐ The amendments are not in compliance with 37 CFR 1.121. See attached Notice of Non-Compliant Amendment (PTOL-324).
5. ☐ Applicant's reply has overcome the following rejection(s): _____.
6. ☐ Newly proposed or amended claim(s) _____ would be allowable if submitted in a separate, timely filed amendment canceling the non-allowable claim(s).
7. ☐ For purposes of appeal, the proposed amendment(s): a) ☐ will not be entered, or b) ☐ will be entered and an explanation of how the new or amended claims would be rejected is provided below or appended.
The status of the claim(s) is (or will be) as follows:
Claim(s) allowed: _____.
Claim(s) objected to: _____.
Claim(s) rejected: _____.
Claim(s) withdrawn from consideration: _____.

AFFIDAVIT OR OTHER EVIDENCE

8. ☐ The affidavit or other evidence filed after a final action, but before or on the date of filing a Notice of Appeal will not be entered because applicant failed to provide a showing of good and sufficient reasons why the affidavit or other evidence is necessary and was not earlier presented. See 37 CFR 1.116(e).
9. ☐ The affidavit or other evidence filed after the date of filing a Notice of Appeal, but prior to the date of filing a brief, will not be entered because the affidavit or other evidence failed to overcome all rejections under appeal and/or appellant fails to provide a showing of good and sufficient reasons why it is necessary and was not earlier presented. See 37 CFR 41.33(d)(1).
10. ☐ The affidavit or other evidence is entered. An explanation of the status of the claims after entry is below or attached.

REQUEST FOR RECONSIDERATION/OTHER

11. ☒ The request for reconsideration has been considered but does NOT place the application in condition for allowance because:
See Continuation Sheet.
12. ☐ Note the attached Information Disclosure Statement(s). (PTO/SB/08) Paper No(s). _____.
13. ☐ Other: _____.

/Randy Gulakowski/
Supervisory Patent Examiner, Art Unit 1796

Continuation of 11. does NOT place the application in condition for allowance because: There is no amendment to the present claims. There is no characteristic of the resulting product. Argument that Jane invention does not teach unplasticized starch having a moisture content of less than about 1% as required in the independent claims 1, 10 and 17 is not persuasive. Jane discloses unmodified starch in granular form. Term unmodified is within the scope of unplasticized. the granular starch are non-sticky=do not adhere to one another, the starch is dry. During the heating the components at 110 to 200 water is evaporated. Thus, a moisture content of less than 1% is inherent for starch. The secondary reference to Dehennau is cited as evidence that polymers serving as the coupling agent possess chemical functional groups which are active towards the hydroxyl functional groups of the starch. The secondary reference to Kozma is cited as evidence for forming covalent bond between the polyethylene and grafted maleic anhydride. The combination of the teachings of the references is proper. In the second rejection, Andersen does disclose unmodified starch in the granular form having the moisture content below to 1% as evidence of available starch having claimed property. Chinnaswamy discloses a covalent bond between the starch and the hydrocarbon chain of the biodegradable polymer. References disclose the known method for creating covalent bond between the maleic anhydride grafted polyethylene and starch. The combination of teachings is proper. Claims 1 and 3-18 are rejected. Claim 19 is withdrawn from consideration as was discussed in the final office action. The examiner apologizes mistakenly mark box 6 in the first page including claim 19.

EXHIBIT C

United States Patent [19]

Jane et al.

[11] Patent Number: 5,115,000

[45] Date of Patent: May 19, 1992

[54] BIODEGRADABLE STARCH PLASTICS
INCORPORATING MODIFIED
POLYETHYLENE

[75] Inventors: Jay-Lin Jane; Alan W. Schwabacher;
Sam N. Ramrattan; Jeffrey A. Moore,
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[73] Assignee: Iowa State University Research
Foundation, Inc., Ames, Iowa

[21] Appl. No.: 540,583

[22] Filed: Jun. 19, 1990

[51] Int. Cl.⁵ C08L 3/00; C08L 23/00;
C08F 8/00

[52] U.S. Cl. 524/47; 525/191;
525/240; 525/252

[58] Field of Search 524/47; 525/191, 252,
525/240

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Primary Examiner—Nathan M. Nutter
Attorney, Agent, or Firm—Zarley, McKee, Thomte,
Voorhees & Sease

[57] ABSTRACT

A composition is disclosed for a biodegradable, blendable plastic having improved tensile strength. It consists of starch, oxidized polyethylene, and polyethylene. The starch is included in an amount up to 50% by weight, the oxidized polyethylene up to 15% by weight, and the remaining amount is polyethylene. It is preferred that high molecular weight oxidized polyethylene be used and in the method of producing the composition. it is preferred that the blending of the components occur at a temperature range of 110° C. to 200° C.

11 Claims, No Drawings

BIODEGRADABLE STARCH PLASTICS INCORPORATING MODIFIED POLYETHYLENE

BACKGROUND OF THE INVENTION

Plastics have become an integral part of our everyday life, and have been used for a multitude of purposes. They are ordinarily light weight, durable, and easily molded into a variety of forms. However, they have a distinct disadvantage in that plastics are usually not capable of self-decomposition. Thus, a tremendous problem exists with most plastics in their continual accumulation and contribution to the increasing waste problems faced in many countries. The problem of disposal of undecomposable plastics has risen to a point of considerable concern.

Polyethylene is among the most common polymers used in the plastics industry. It has high tensile strength and a high melting point which provides for good blending and easy extrusion into various forms. It is especially useful in making plastic films, which are used in items such as garbage bags. It has the disadvantage of most plastics, however, in not being biodegradable.

Attempts have been made to create plastics which are biodegradable by incorporating starches into polymers. This, however, has contributed its own unique problems. Starch is hydrophilic, while polyethylene is hydrophobic, and so the two are not compatible with one another. Furthermore, when more starch is introduced into a polymer, the resulting plastic film will typically have poor tensile strength.

It would be a considerable advantage to develop a plastic incorporating starch which overcomes the problems of the incompatibility between polyethylene and starch, the loss in tensile strength with the increase in the amount of starch, and still have a product which is easily blended and extruded into the desired form. This invention relates to such an improvement.

Accordingly, it is an object of the invention to provide for a biodegradable plastic having good tensile strength.

Another object of the invention is to provide for a plastic from polyethylene in which the polyethylene is made compatible with starch.

Still another object of the invention is to provide for a plastic which is easily capable of being blended and extruded into a desired form.

Yet another object of the invention is to provide for a plastic which is relatively inexpensive to manufacture.

Still further objects of the invention will become apparent through the following disclosure.

SUMMARY OF THE INVENTION

A blendable, high tensile strength, biodegradable plastic is disclosed which consists of starch, oxidized polyethylene and unmodified polyethylene. The components are blended while heated at a temperature of 110° C. to 200° C. The starch comprises up to 50% of the composition, the oxidized polyethylene comprises up to 15% of the composition, and the remaining amount is the polyethylene. The resulting mixture after heating and blending may be formed into the desired shape, and is especially useful for plastic films.

DETAILED DESCRIPTION OF THE INVENTION

The composition of this invention consists of starchy material, oxidized polyethylene and polyethylene.

The starch which may be used in this invention is preferably a granular starch. Gelatinized starch is not only not necessary, preparation of gelatinized starch is energy consuming, and so granular starch is the preferred component in this invention. Any type of starch may be used, and the term starchy material includes unmodified starches, modified starches, or starch components such as amylose or amylopectin. Native unmodified starches include the cereal grains and root crop starches. There are a variety of modified starches, such as octenyl succinate particle starch for example. However, an advantage of this invention is that native starch may be used and it is not necessary to use modified starch, which is more expensive.

Polyethylene which has been oxidized is the second component of this invention. The manner in which the polyethylene has been oxidized is not critical, and oxidized polyethylene is available commercially. The oxidized polyethylene used in the example below was obtained from the Aldrich Company at 940 West St. Paul Avenue, Milwaukee, Wisconsin 53233. The third component is polyethylene which has not been so modified.

The oxidized polyethylene provides a considerable advantage. As has been noted, since polyethylene is hydrophobic and starch is hydrophilic, the two are usually incompatible. However, with the addition of the oxidized polyethylene, a "bridge" is formed which connects the starch with polyethylene. Oxidized polyethylene has carboxy groups and ketone groups. While not wishing to be bound by any theory, it is the belief of the inventors that the carboxyl groups on the oxidized polyethylene form ester bonds with the hydroxyl groups on the starch to an extent determined by processing. This, along with hydrogen bonding, provides for compatibility between the polyethylene and the starch. This has additionally been associated with improved tensile strength. Finally, a third improvement results because of addition of the oxidized polyethylene. The carboxyl groups on the oxidized polyethylene enables a variety of organisms to degrade the polymer by beta-oxidation, in direct contrast to other carboxyl containing polyethylenes such as ethylene acrylic acid copolymer. Thus, the presence of the oxidized polyethylene further enhances biodegradation of the material, in addition to that already provided by the starch itself.

Oxidized polyethylene is advantageous in that it is not highly acidic and no neutralizer is required. It may be used with granular starch without difficulty. It also is less expensive than other polymers, such as ethylene acrylic acid copolymer.

While providing these advantages, the addition of oxidized polyethylene has several disadvantages. Oxidized polyethylene and starch alone does not provide for the best possible tensile strength. Additionally, oxidized polyethylene has a lower melting point than polyethylene. Because of this low melting point, difficulties are encountered in blending the composition.

One method of overcoming the problems associated with low melting point of the oxidized polyethylene is to provide that the polyethylene which has been oxidized has a high molecular weight. Low molecular weight polyethylene has been defined as that having a molecular weight range from about 2000 to about 5000

grams per mole. High molecular weight polyethylene would have a molecular weight in excess of this. With the higher molecular weight, the melting point increases and blendability improves.

However, even better tensile strength and higher melting point may be achieved by adding polyethylene to the oxidized polyethylene and starch. By virtue of adding unmodified polyethylene, the melting point will increase, and blendability improve. The tensile strength will improve even further. Unmodified polyethylene also has the advantage of being lower in cost than oxidized polyethylene.

Thus, by combining starch, oxidized polyethylene, and unmodified polyethylene, one may produce a blendable, biodegradable plastic having greatly improved tensile strength.

The actual process for the blending of the materials will vary depending upon the mechanism used. The type of device used for the blending is not critical. However, it has been found that among the most popular methods of blending, batch mixing and screw extrusion, that screw extrusion provides more cost effective and time efficient results. In either process, the three components are blended together. Starch may be added into the composition up to 50%. When tensile strength is desired to be the property most emphasized the preferred range of the amount of starch to use is between 6% and 15% by weight. The preferred range may vary when other properties are emphasized. For example, higher amounts of starch are preferred when biodegradability is the property most emphasized. When used in creating a plastic film, the industry typically includes starch in the amount of 6% by weight to 9% by weight. In fact, there is no minimum amount of starch within this range. Inclusion of any amount of starch will improve biodegradability. However, as noted, when the amount of starch exceeds 50%, tensile strength is considerably reduced. This is because the granules disrupt continuity of the polymers and strength drops. Typically, the goal in the industry is to use as much starch as possible without unnecessarily sacrificing tensile strength. With this invention, it is possible to increase the amount of starch while still retaining good tensile strength.

It has been found that the preferred range of inclusion of oxidized polyethylene is between 6% to 15% by weight. When less than 6% is used it is ordinarily too little to serve the purpose; if more than 15% is used problems with blending are often encountered. The ratio of the amount of starch to oxidized polyethylene falls within the range of 1:1 starch to oxidized polyethylene, up to about 3.3:1 starch to oxidized polyethylene. The remaining amounts of the composition consist of the polyethylene.

In a batch mixing process, it has been found that the preferred temperature range for low molecular weight oxidized polyethylene inclusion is between 110° C. to 130° C. When high molecular weight oxidized polyethylene is used in the batch process the temperature range falls within 150° C. to 170° C. The die temperatures on

the extruder when compounding are preferably set at 150° C. for low molecular weight oxidized polyethylene, and 165° C. for high molecular weight oxidized polyethylene.

In the preferred screw extruder process, the temperature range for the compound blending ranges between 145° C. to 165° C. Ordinarily, the blending occurs at about 40 rpm. A double screw extrusion mechanism provides even better mixing at this point. The result of the first blending and extrusion is that the compound is formed into a rod shape, and then cut into pellets. In the second step of the process, the pellets are blended and heated at even higher temperatures. The composition is heated to a molten state, and the preferred temperature range at this point is 150° C. to 200° C., with the typical mixing speed at 20 to 26 rpm. Following this, the composition continues to a blowing tower where it is then blown into a film.

These are only two mechanisms for blending and extruding. Other mechanisms are known to those skilled in the art.

The time for heating and blending to occur is not critical to the process and those skilled in the art will recognize that the parameters will vary depending on the mechanisms used. With a screw extruder, for example, one calculates the mixing time by determining the length of the barrel and dividing this by the number of flights to obtain the pitch. The revolutions per minute are multiplied by the pitch to obtain the screw speed. The length of the barrel is divided by the screw speed to obtain the mixing time. For instance, in the example below, barrel length was 31.24 inches, and there were 25 flights yielding a pitch of 1.25 inches. At 15 rpm, the screw speed was 18.75 inches per minute, and the mixing time calculated at 2.14 minutes.

The following example is set forth for illustrative purposes only and is not intended to limit the invention.

EXAMPLE

The following data reflected in the table below results from a blending and heating process using the double screw and single screw extruders as described above.

As can be seen from the table below, four different compositions were tested. In each test, the amount of native starch, to oxidized polyethylene, to polyethylene in the mixture is shown. The compound blending parameters are set forth, including the rpm, and the temperature range used. The first column of the temperature zone readings shows temperatures measured from a probe placed within the feeding zone, the second and third indicate temperature probes in the barrel, while the last shows a temperature probe at the exit point. Extrusion parameters are also set forth, which also include zone temperatures and rpm. These are higher temperatures and a molten state results. As can be seen, it is preferred that the temperature increase as the composition moves toward the exit port in the compound and extrusion steps.

TABLE

		COMPOUNDED PARAMETERS		EXTRUSION PARAMETERS		S.D. PSI	\bar{X} PSI	S.D. % ELONG.	\bar{X} % ELONG.
		RPM	ZONE TEMP. °C.	RPM	ZONE TEMP. °C.				
TEST 1	7% NS/7% OPE/ 86% PE	40	145,155,160,165	26	150,160,200	447	2407	67.5	523.2
TEST 2	15% NS/15% OPE/ 70% PE	40	145,155,160,165	25	150,160,200	442	2330	30.4	580.7

TABLE-continued

		COMPOUNDED PARAMETERS		EXTRUSION PARAMETERS		S.D.	\bar{X}	S.D. %	\bar{X} %
		RPM	ZONE TEMP. °C.	RPM	ZONE TEMP. °C.	PSI	PSI	ELONG	ELONG.
TEST 3	25% NS/15% OPE/ 60% PE	40	150.155.160.165	20	150.155.160.170.200	267	1383	66.4	466.0
TEST 4	50% NS/15% OPE/ 35% PE	40	150.155.160.165	20	150.155.160.170.200	160	665	54.8	88.5
CONTROL 1	PE/7% NCS	40	150.155.160.165	20	150.155.160.170.200	710	2193	79.0	542.9
CONTROL 1	PE/15% NCS	40	155.160.170.185	20	150.155.160.170.200	616	1611	111.7	242.2

Results are shown in the column at the right hand side of the table. The term S.D. PSI refers to the standard deviations in pounds per square inch of measurements obtained; the reference to \bar{X} PSI refers to the average PSI obtained from 15 different samples. The next two columns refer to the standard deviations in percent of elongation, and average percent elongation from testing of 15 samples.

These results may be compared with the control also set forth in the table, wherein native starch was mixed with polyethylene alone. As can be seen, improved tensile strength results from the inclusion of all three components.

Therefore it can be seen that the invention accomplishes at least all of its objectives.

What is claimed is:

1. A blended, high tensile strength, biodegradable plastic composition comprising a starchy material, oxidized polyethylene and unmodified polyethylene the ratio of said starchy material to said oxidized polyethylene being within the range of 1:1 up to about 3.3:1.

2. The composition of claim 1 wherein the starchy material is selected from the group consisting of unmodified starch, modified starch, amylose and amylopectin.

3. The composition of claim 1 wherein the starchy material comprises up to 50% by weight of the composition.

4. The composition of claim 3 wherein the starchy material comprises 6% by weight to 15% by weight of the composition.

5. The composition of claim 1 wherein the oxidized polyethylene is a high molecular weight polyethylene.

6. The composition of claim 5 wherein the oxidized polyethylene has a molecular weight of more than 5000 grams per mole.

7. The composition of claim 1 wherein the oxidized polyethylene comprises up to 15% by weight of the composition.

8. The composition of claim 1 wherein the ratio of starchy material to oxidized polyethylene is in the range of 1:1 up to about 3.3:1.

9. The composition of claim 1 wherein the ratio of starchy material to oxidized polyethylene is 1:1.

10. The composition of claim 1 wherein the starchy material is 6% by weight to 15% by weight of the composition, the oxidized polyethylene is 6% by weight to 15% by weight of the composition and the remaining amount of the composition is polyethylene.

11. A blendable high tensile strength composition for biodegradable films comprising:

a granular starchy material;
polyethylene in an amount sufficient to increase tensile strength and blendability; and
oxidized polyethylene in an amount sufficient to improve binding to the starch and tensile strength the ratio of starchy material to oxidized polyethylene being within the range of 1:1 up to about 3.3:1.

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EXHIBIT D

United States Patent [19]**Dehennau et al.**[11] **Patent Number:** **5,510,401**[45] **Date of Patent:** **Apr. 23, 1996**[54] **STARCH-BASED COMPOSITION**[75] Inventors: **Claude Dehennau; Thierry Depireux**,
both of Waterloo, Belgium[73] Assignee: **Solvay (Société Anonyme)**, Brussels,
Belgium[21] Appl. No.: **227,230**[22] Filed: **Apr. 12, 1994****Related U.S. Application Data**

[63] Continuation of Ser. No. 14,679, Feb. 8, 1993, abandoned.

[30] **Foreign Application Priority Data**

Feb. 7, 1992 [BE] Belgium 09200130

[51] **Int. Cl.⁶** **C08L 3/00; C08L 89/00;**
C08K 5/10; C08K 5/05[52] **U.S. Cl.** **524/47; 524/312; 524/387**[58] **Field of Search** **524/47, 312, 387**[56] **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—Paul R. Michl*Assistant Examiner*—La Vonda R. DeWitt*Attorney, Agent, or Firm*—Spencer & Frank[57] **ABSTRACT**

The invention relates to an alloy composition possessing improved properties of mechanical resistance. The composition contains a starch, which is preferably plasticised, and a polymer which acts as coupling agent which is chosen from the group consisting of polyolefins modified by chemical functional groups which are active towards the hydroxyl functional groups of starch.

Generally, the composition also contains a thermoplastic polymer.

The invention also relates to the process for preparing this composition and the use of these compositions for the manufacture of films intended for the paper market and for packages made from biodegradable plastic.

18 Claims, No Drawings

STARCH-BASED COMPOSITION

This application is a Continuation of application Ser. No. 08/014,679, filed Feb. 8, 1993, now abandoned.

SUBJECT OF THE INVENTION

The present invention relates to a composition based on optionally plasticised starch possessing improved properties, especially of transparency and of mechanical resistance, by virtue of the presence of a coupling agent optionally comprising a thermoplastic polymer.

The invention also relates to the process for preparing the composition according to the invention and to its use.

STATE OF THE ART AND TECHNOLOGICAL BACKGROUND

Starch constitutes an important source of macromolecules since it is renewable by means of the photosynthesis cycle, and it is available in large amounts, is biodegradable and is inexpensive.

Owing to its chemical and physical structure, starch is not intrinsically a thermoplastic and it is mainly used in water-based preparations as a binder, thickener or foodstuff.

Attempts have therefore been made to modify starch by plastifying it and/or by subjecting it to an appropriate heat treatment so as to render it workable at high temperature.

The use of a starch which is structurally modified during a preliminary processing such as an extrusion and, optionally, the addition of water, which renders the final product mouldable at high temperature, has been proposed in European Patent Application EP-A-0 304 401 (Warner Lambert Co.).

Additional components such as plasticisers comprising polyalkylene glycol or glycerol acetate can also be incorporated into structurally modified starch.

The use of another structurally modified starch, whose viscosity has been reduced by means of a depolymerisation catalyst, is proposed in European Patent Application EP-A-0 282 451 (Warner Lambert Co.).

Additional components such as plasticisers, diluents or fillers can also be incorporated into starch.

The extrusion of thermoplastic starch in the form of a mixture of a starch, which is at least partially crystalline, with water and/or other additives such as glycerine (5 to 35% by weight relative to the total weight of the mixture), which reduce its melting point (see page 27, lines 1 to 7 and claim 13), is known from the document WO-90 10 019 (Tomka).

A technique for heating and mixing starch with other additives which permit melting of the starch at a temperature lower than its decomposition temperature, is known from patent application WO-90 05 161 (Tomka).

However, starch which is treated by these processes remains a hydrophilic material which absorbs water, which plasticises it and causes it to lose all mechanical properties. This constitutes a major obstacle to a mass use of this product, although the hydrophilic character also constitutes a property which is essential for good biodegradability.

Research studies have therefore also been carried out in order to reduce the sensitivity of starch to water, especially by coating the starch with a hydrophobic compound.

European Patent Application EP-0 378 646-A (Tomka) (equivalent to WO-90 00 1043) describes the coating of a hydrophilic polymer such as starch or gelatine with a film-forming hydrophobic compound consisting of polyhydroxycarboxylic acid, optionally supplemented with proteins, natural lipids, wax and/or paraffin.

The document "Starch-based film for Degradable Agricultural Mulch" (Ind. Eng. Chem. Prod. Res. Develop. vol. 13 (1), 1974, p. 90) describes a coating with polyvinyl chloride (PVC) or with a vinylidene chloride and acrylonitrile copolymer, of a film of starch supplemented with polyvinyl alcohol (PVA) and cross-linked with formaldehyde.

Mixtures of starch with copolymers have also been described in the following documents:

U.S. Pat. No. 4,133,784 (U.S. Secretary of Agriculture) and the document "Composites of starch and polyethylene coacrylic acid, complexing between polymer components", (Journal of Applied Polymeric Science, vol. 40, pp. 811 to 821, 1990) mention a composite material based on starch and an ethylene and acrylic acid (EAA) copolymer which is described as being stable under atmospheric conditions only for limited periods of time.

Patent EP-0 408 503-A (Warner Lambert Co.) describes a composite material consisting of structurally modified starch and ethylene-vinyl alcohol type (EVOH) copolymers and optionally a thermoplastic polymer which is insoluble in water.

However, the products obtained are found to be fragile and tear easily directly after their processing, and during storage they soften with the absorption of water and the plasticisation which it produces.

OBJECT OF THE INVENTION

The invention is intended to provide a composition based on a starch modified by the addition of a so-called polymer coupling agent which confers on the thermoformed starch improved properties, in particular improved properties of transparency, tear strength and reduced bleaching during folding.

Additionally, the present invention is intended to provide an agent which acts as compatibility-promoting agent for a mixture of starch with a thermoplastic polymer and which enhances the mechanical resistance properties of the said mixture.

CHARACTERISTIC FEATURES OF THE INVENTION

The addition to starch of polymers such as polyolefins which reduce the penetration of water by their natural hydrophobicity, can be envisaged so that these mixtures possess improved properties of resistance to moisture. Mixtures of this type, in particular mixtures of polyolefins and starch are however very heterogeneous since very polar starch is incompatible with an apolar polyolefin.

According to the invention, an alloy composition is proposed which possesses improved properties of transparency and mechanical resistance, comprising a starch and a polymer acting as coupling agent which is chosen from the group consisting of polyolefins modified by chemical functional groups which are active towards the hydroxyl functional groups of starch, which is characterised in that the ratio of its dynamic modulus of elasticity G' to its dissipative modulus G'' , measured at 160° C. and at a frequency of 0.1 rad per

s (0.1 s^{-1}), is greater than 1.6, and preferably greater than 1.7.

Details on the measurement and the physical significance of the G' and G'' moduli are given in a description below of the preferred embodiments of the invention.

According to a preferred embodiment of the invention, the polymer which acts as coupling agent is chosen from the group consisting of polyolefins modified by grafting maleic anhydride, and of ethylene copolymers and terpolymers containing units derived from maleic anhydride.

The use of starch supplemented with a plasticiser, in particular glycerine, diglycerine, polyglycerine and/or sorbitol, can prove to be advantageous in many cases.

According to another preferred embodiment of the invention, the composition also comprises a thermoplastic polymer which is preferably a polyolefin such as polyethylene.

The starches used are of natural and plant origin. These carbohydrates are mainly composed of amylose and/or amylopectin which occur in variable amounts depending on their biological origin. They may be structurally modified, pregelatinised or modified after the addition of water and/or a plasticiser as described above according to the process described in patent application WO-90 10 019 (Tomka).

By way of non-limitative example, the starch may be a normal maize starch, a maize starch high in amylose (EURYLON 7® from Roquette), a maize starch high in amylopectin (Waxilys® from Roquette), a wheat starch (Nutralys® from Roquette), a potato starch or a mixture thereof.

Preferably, the starch used in the compositions of the invention is a starch whose amylopectin content is greater than 70%, which makes it possible to obtain products which are more transparent, colourless and non-sticky after retaining water on contact with atmospheric moisture.

The values of the percentages by weight of the various components of the alloy according to the invention are respectively of the order of 20 to 80%, and preferably 40 to 60% of starch, preferably plasticised starch, 0 to 70%, and preferably 30 to 50% of thermoplastic polymer, and 1 to 30%, preferably 5 to 20% of coupling agent.

When plasticised starch is used, it may contain up to 50% by weight of plasticiser, preferably, however, of the order of 5 to 40% by weight of plasticiser, expressed relative to the total weight of the starch and the plasticiser.

The polymers serving as the coupling agents used in the compositions according to the invention are, as already indicated, compounds which possess chemical functional groups which are active towards the hydroxyl functional groups of the starch.

These polymers are not very crystalline and have a melting point of less than 150°C .

Advantageously, the coupling agent can also be used to make a thermoplastic polymer starch-compatible.

The addition of a thermoplastic polymer, in particular a polyolefin such as polyethylene which reduces the penetration of water by virtue of its natural hydrophobicity, gives an alloy which possesses improved moisture resistance properties.

In the compositions containing 20 to 80%, preferably 40 to 60% of plasticised starch, the incorporation of 10 to 70%, preferably 30 to 50% of a thermoplastic polymer, and of 1 to 30%, preferably 5 to 20% of a compatibility-promoting agent, also makes it possible to increase the breaking elongation properties, at various temperatures, of the products of the invention.

Another aspect of the invention relates to a process for preparing a starch-based composition in which a plasticisa-

tion means is supplied with a mechanical mixture containing the coupling agent, the starch supplemented with a plasticiser which may be precompounded, and optionally a thermoplastic polymer. The plasticisation means may be a co-rotating twin screw extruder equipped with one or more degassing vents or an inner mixer which melts the mixture. The starch may be either dried or not before being incorporated into the mixture, and it may be in a form of a powder impregnated with plasticiser or in the form of granules which are plasticised during a preliminary compounding operation.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The products entering into the compositions of the invention are melted and homogenised with a co-rotating twin screw extruder or a laboratory Brabender® plastograph inner mixer according to the conditions described in the examples below.

Rheological measurements are then carried out on a 1 mm thick plate obtained by hot pressing the mixtures thus produced and drying at 70°C . under vacuum for 12 hours.

The rheological measurements show that the formulations which are most resistant to tearing, which are the least bleached during folding and which are most transparent, are those which have a ratio of their dynamic modulus G' , representative of their elastic response (shear storage modulus), to their dissipative modulus G'' (shear loss modulus), measured at a temperature of 160°C . and at a frequency of 0.1 rad per second (0.1 s^{-1}), greater than 1.6 and preferably greater than 1.7, and that the choice of maleic anhydride-containing copolymer or terpolymer is advantageous.

The physical significance of the G' and G'' moduli, the expressions linking them and other details relating to them have been described in the document "Viscoelastic properties of polymers" by J. D. Ferry, 2nd edition, John Wiley & Sons, Inc. 1970 (pages 12 to 15).

The G' and G'' moduli are evaluated at 160°C . using a rheometer which makes it possible to measure the dynamic mechanical properties of the polymers from the glassy or crystalline state to the molten state. The measurements in the molten state are carried out on tablets 1 to 2 mm thick and 2.5 cm in diameter taken from plates which are pressed from the compositions according to the invention.

The measurement consists in determining, at a frequency of 0.1 rad per second (0.1 s^{-1}), at a temperature of 160°C ., the G' and G'' moduli on the various alloy compositions of the invention, on a common base formula containing 75% by weight of starch+plasticiser and 25% by weight of compatibility-promoting agent.

The examples below illustrate the invention.

Example 1 (reference)

38.9 g of starch is mixed with 13.6 g of glycerine and 17.5 g of Dowlex® low density linear polyethylene type 4000E. This mixture is introduced into a laboratory Brabender® plastograph inner mixer heated to a constant temperature of 160°C . and then mixed for 10 minutes at a cam rotating speed of 50 revolutions/minute. After the mixing, the molten mass is collected. After it has cooled, a portion of it is collected and pressed in a press, either with a thickness of 0.35 mm in order to evaluate the transparency, the homogeneity and the tear strength on the one hand, or with a thickness of 1 mm in order to evaluate the G' and G'' moduli by means of a Rheometrics® rheometer and at a temperature

of 160° C. At 0.1 s⁻¹, the G'/G'' ratio is 1.15. The film obtained is found to be heterogeneous and to tear easily.

Example 2 (reference)

The procedure is the same as in Example 1 except that LLDPE is replaced by an ethylene/acrylic and methacrylic acid copolymer containing 26% of Escor® acrylic and methacrylic acid type ATX 325. The G'/G'' ratio is equal to 1.34 and the films obtained tear easily.

Example 3 (reference)

The procedure is the same as in Example 1 except that LLDPE is replaced with a Lotryl® ethylene/acrylic ester copolymer type 3400. The G'/G'' ratio is equal to 1.27 and the films are heterogeneous and fragile.

Example 4

The procedure is the same as in Example 1 except that LLDPE is replaced with Admer® maleic anhydride-grafted polyethylene type L2100. The G'/G'' ratio is equal to 1.67 and the films obtained are homogeneous, resistant to tearing but become bleached at the position of a fold.

Example 5 (reference)

The procedure is the same as in Example 1 except that LLDPE is replaced with a Lotader® ethylene/acrylic ester/maleic anhydride terpolymer type 3700. The G'/G'' ratio is 1.47; the films tear and are heterogeneous.

Example 6

The procedure is the same as in Example 1 except that a type 3410 Lotader® is used. The G'/G'' ratio is 1.71 and the films are homogeneous, are difficult to tear and do not bleach at the position of a fold.

Example 7

The procedure is the same as in Example 1 except that a type 3200 Lotader® is used. The G'/G'' ratio is 2.11 and the films are homogeneous, resistant to tearing and do not bleach at the position of a fold.

Example 8 (reference)

The procedure is the same as in Example 1 except that a Rexpearl® ethylene/glycidyl methacrylate copolymer type RA3150 is used. The G'/G'' ratio is 1.45 and the films obtained tear and are heterogeneous.

Example 9 (reference)

The procedure is the same as in Example 1 except that a Rexpearl® ethylene/glycidyl methacrylate/acrylic ester terpolymer type JS4450 is used. The G'/G'' ratio is 1.38 and the films tear and are heterogeneous.

Example 10

The compound obtained in Example 7 is granulated. 42 g of these granules are mixed with 28 g of Dowlex® linear low density polyethylene type 4000E. The mixture is subjected to the same procedure as that described in Example 1. The films obtained are homogeneous, do not tear and do not become bleached at the position of a fold.

Example 11

The compound obtained in Example 6 is granulated. 42 g of these granules are mixed with 28 g of Dowlex® linear low density polyethylene type 4000E. The films obtained are homogeneous, do not tear and do not become bleached at the position of a fold. The percentage of breaking elongation measured, after the water regain has stabilised, at 23° C., with an IVSTRON apparatus (speed 100 mm/minute), is 90%, and at 190° C., with a Rheometrics® elongational viscosimeter (speed gradient=0.5 s⁻¹) is 1420%.

Example 12 (reference)

The same test as that of Example 11 is carried out except that the compound prepared in Example 1 is used as starting material. The films obtained tear and are heterogeneous. The percentage of breaking elongation, measured under the same conditions as that for Example 11, is 41% at 23° C. and 346% at 190° C.

Example 13

34.125 g of Roquette® normal, native and non-dried maize starch (12.5% by weight of water) are mixed with 18.375 g of glycerine and with 17.5 g of Lotader® 3200. The mixture is mixed and processed according to the procedure used in Example 1. The G'/G'' ratio is 1.95 and the quality of the films obtained is equivalent to that observed during examination of the films of Example 7.

Example 14

22.75 g of Roquette® normal, native and non-dried maize starch (12.5% by weight of water) are mixed with 12.25 g of glycerine, 28 g of Dowlex® 4000E and 7 g of Lotader® 3200. The whole is mixed and processed according to the procedure used in Example 1. The quality of the films is equivalent to that of the films of Example 10.

The products obtained can be used for the manufacture of films intended for the paper market or for packages made from biodegradable plastic.

We claim:

1. A composition, comprising a starch and a polymer acting as coupling agent which is chosen from the group consisting of polyethylene modified by grafting maleic anhydride, and terpolymers containing units derived from maleic anhydride, the ratio of the dynamic modulus of elasticity G' of said composition to the dissipative modulus G'' of said composition, measured at 160° C. and at a frequency of 0.1 rad per s (0.1 s⁻¹), being greater than 1.6.

2. The composition according to claim 1, wherein the G'/G'' ratio is greater than 1.7.

3. The composition according to claim 1, wherein the starch is plasticised with a plasticiser selected from the group consisting of glycerine, diglycerine, polyglycerine, sorbitol, a polyol and mixtures thereof.

4. The composition according to claim 1, further comprising a polyethylene.

5. The composition according to claim 1, wherein the starch used is destructured or pregelatinised.

6. The composition according to claim 1, wherein the starch contains more than 70% by weight of amylopectin.

7. The composition according to claim 4, wherein said composition comprises from about

20 to 80% by weight of starch, from about 0 to 70% by weight of polyethylene and

from about 1 to 70% by weight of coupling agent.

8. The composition according to claim 5, wherein the starch used contains up to about 50% by weight of plasticiser expressed relative to the total weight of the starch and the plasticiser.

9. A biodegradable film comprising a composition according to claim 1.

10. A process for preparing a composition, comprising starch and a polymer acting as a coupling agent which is chosen from the group consisting of polyethylene modified by grafting maleic anhydride, and terpolymers containing units derived from maleic anhydride, the ratio of the dynamic modulus of elasticity G' of said composition to the dissipative modulus G'' of said composition, measured at 160° C. and at a frequency of 0.1 rad per s (G'/G''), being greater than 1.6, said process comprising plasticising a mixture comprising the coupling agent and starch.

11. The process according to claim 10, wherein said mixture is plasticised with an inner mixer.

12. The process according to claim 10, wherein the plasticisation means is a co-rotating twin screw extruder.

13. The process according to claim 10, wherein a mixture is used which comprises a plasticised starch compound and a coupling agent.

14. The process according to claim 10, wherein a mixture is used which comprises a native, pregelatinised or modified starch, a plasticiser and a coupling agent.

15. A process for preparing a biodegradable film, comprising the process defined in claim 10.

16. A composition, comprising a starch and a polymer acting as coupling agent, selected from the group consisting of polyethylene modified by grafting maleic anhydride, and terpolymers containing units derived from maleic anhydride, the ratio of the dynamic modulus of elasticity G' of said composition to the dissipative modulus G'' of said composition being greater than 1.6.

17. A process for preparing a composition comprising starch and a polymer acting as a coupling agent, selected from the group consisting of ethylene modified by grafting maleic anhydride, and terpolymers containing units derived from maleic anhydride, the ratio of a dynamic modulus of elasticity G' of said composition to the dissipative modulus G'' of said composition being greater than 1.6, said process comprising plasticising a mixture comprising the starch and coupling agent.

18. The process according to claim 17, wherein said mixture is plasticised with an inner mixer.

* * * * *

EXHIBIT E

(12) **United States Patent**
Kozma et al.

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(45) **Date of Patent:** **Jun. 5, 2001**

(54) **POLYMER ARTICLES INCLUDING MALEIC ANHYDRIDE AND ETHYLENE-VINYL ACETATE COPOLYMERS**

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(51) Int. Cl.⁷ **C08F 8/00; C08F 2/46**

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(58) Field of Search **525/193; 521/134; 522/109, 120**

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(57) **ABSTRACT**

Polymer articles including ethylene-vinyl acetate and maleic anhydride are described. The ethylene-vinyl acetate can be a high vinyl acetate content ethylene-vinyl acetate. The articles include foamed articles and non-foamed articles. The foamed articles have improved characteristics and properties, such as surface bonding properties.

44 Claims, No Drawings

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POLYMER ARTICLES INCLUDING MALEIC ANHYDRIDE AND ETHYLENE-VINYL ACETATE COPOLYMERS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of U.S. Ser. No. 09/003,223, filed Jan. 6, 1998, which is a continuation-in-part of U.S. Ser. No. 08/749,740, filed Nov. 15, 1996 U.S. Pat. No. 5,883,144.

BACKGROUND OF THE INVENTION

The invention relates to foamed articles and non-foam flexible materials formed from ethylene-vinyl acetate copolymers and maleic anhydride.

Ethylene-vinyl acetate (EVA) copolymers provide materials that can be processed like other thermoplastics, but which approach a rubbery character in softness and elasticity. EVA copolymers are generally soft materials. However, materials containing EVA copolymers can be difficult to process due to the tackiness of the material.

Generally, polymer materials can be used to produce a variety of articles including foams. Foamed polymeric materials have a variety of uses. For example, natural rubber latex foams provide soft materials for body contact and the application of cosmetics. Polyvinyl chloride (PVC) plastisol foams can have a soft, durable feel that simulates leather to the touch. Open cell foams based on polyurethanes have been made suitable for many applications, such as cushions for packaging, automotive applications, home bedding, filters (e.g., for air conditioners), applicators (e.g., for shoe polish), or sound attenuating panels (e.g., for rooms or speakers).

SUMMARY OF THE INVENTION

In one aspect, the invention features a polymer article including a mixture having a maleic anhydride grafted component and an ethylene-vinyl acetate copolymer. A portion of the mixture is cross-linked (e.g., sufficiently crosslinked to form a flexible polymer article having low tackiness). The mixture can be foamed or non-foamed. In non-foamed articles, the maleic anhydride grafted component can be a polyolefinic polymer.

In another aspect, the invention features a method of making a polymer article. The method includes providing a mixture including an ethylene-vinyl acetate copolymer and maleic anhydride, and cross-linking the mixture sufficiently to form the polymer article. The maleic anhydride is grafted to a portion of the mixture. The mixture can be expanded to form a foamed article. The cross-linking can be peroxide, silane cross-linking, radiation cross-linking, or combinations thereof. The peroxide can be dicumyl peroxide.

The polymer article generally has low tackiness and is flexible. The mixture can include an ethylene-vinyl acetate copolymer, a polyolefinic polymer, or a mixture thereof.

A polymer article having low tackiness has a low degree of self sticking. In other words, a low tackiness material substantially does not stick to itself. Foamed materials having low tack do not block. For example, the materials do not block when surfaces of two foam pieces slide over each other without sticking to each other.

A flexible article bends readily without cracking or permanently deforming. The flexibility of an article can be tested by measuring the compression deflection of the article according to ASTM-3575.

The vinyl acetate content of the ethylene-vinyl acetate copolymer can be between about 9 and about 60 percent, preferably between about 15 and about 50 percent, and more preferably between about 15 and about 35 percent.

The polyolefinic polymer can be grafted with maleic anhydride. In other embodiments, the ethylene-vinyl acetate copolymer can be grafted with maleic anhydride. The method can include grafting maleic anhydride to the polyolefinic polymer, the ethylene-vinyl acetate copolymer, or combinations thereof.

The article can include between about 1 and about 90 weight percent of a maleic anhydride grafted polyolefinic polymer, preferably between about 5 and about 30 weight percent, and more preferably between about 5 and about 15 weight percent. The maleic anhydride content of the grafted polyolefinic polymer can be between about 0.01 and about 10 weight percent, preferably between about 0.5 and about 2.0 weight percent.

In preferred embodiments, the article is a foamed article. The foamed article can be an open cell or closed cell foam. The article can have a foam density between about 1.5 and 50 pounds per cubic foot. When the article is a closed cell foam, the foam can have a 25% compression deflection of less than 3 psi. In other preferred embodiments, the article is non-foamed. The non-foamed article is flexible and has low tackiness. The foamed and non-foamed article can be suitable for use in, for example, wire and cable applications. The article can be a bead or particulated foam.

The article can be expanded to form a foam. Expansion of the mixture can include free expansion or compression molding of the mixture. Expanding can take place before cross-linking, during cross-linking, and/or after cross-linking. Compression molding can include the steps of pressing the polymer mixture using a high tonnage press at a temperature of between 240 and 480° F. (e.g., between 275 and 320° F.) and a pressure of between 50 and 5000 psi (e.g., between 250 and 2500 psi) for between 20 and 90 minutes followed by heating the polymer mixture at a temperature between 300 and 380° F.

The foamed material can be crushed after expansion to form an open cell foamed article. A coating, an adhesive, or a laminated layer can be applied to a surface of the article, or the article can be dipped to form a layer on the surface of the article.

The mixture can include other resins, foaming agents, cross-linking agents, activators (e.g., between 0.1 and 5 weight percent), foaming agents (e.g., between 2 and 50 weight percent), particulate fillers, fibrous fillers, antioxidants, ultraviolet stabilizers, thermal stabilizers, pigments and colorants, cell-growth nucleants such as talc, cell-structure stabilizers such as fatty acids or amides, property-modifiers, processing aids, additives, fire retardants, antistatic components, antimicrobial components, or catalysts to accelerate cross-linking and other reactions.

In another aspect, the invention features a method of manufacturing a foamed polymer article. The method includes providing a mixture including an ethylene-vinyl acetate copolymer and maleic anhydride grafted to a portion of the mixture, cross-linking the mixture sufficiently to form a flexible polymer article having low tackiness, and expanding the mixture to form a foamed polymer article in a vertical oven. The cross-linking can be silane, peroxide, or irradiation cross-linking, or a combination thereof. The foamed polymer article has a thickness between about 0.015 and 1/8 inch and a density between about 1.5 and 40 pounds

per cubic foot. The method can include applying an adhesive to a surface of the foamed polymer article. The maleic anhydride can improve bonding to the adhesive.

An open cell foam is a foam where there is an interconnection between cells in the foam. There can be greater than about 10 percent open cells (i.e., between 10 and 50 percent) in an open cell foam article, preferably greater than 40 percent, more preferably greater than 80 percent, and most preferably greater than 90 percent. The amount of open cells in a foam can be increased by crushing the foam. A crushed open cell foam can have between 50 and about 98 percent open cells.

A closed cell foam has a predominance of closed cells. For example, a preferred closed cell foam can have 70% or greater closed cells.

The open cell content of a foam can be determined by measuring the amount of water that is absorbed into the foam when the foam is immersed in water. Another method is a gas-volume method using a pycnometer, such as a Quantachrome Model 1000 pycnometer, which measures the percentage of open cells according to method ASTM D-2858.

A low-density polyethylene, or LDPE, is a polymer of ethylene with a density typically between 0.915 and 0.930 g cm⁻³. LDPE resin densities directly relate to the resulting bulk property stiffness. This can limit the degree of mechanical flexibility in foam structures thereof since the lower limit of secant moduli for LDPE is about 20 ksi. While processability of LDPE is quite good, the physical properties, in particular the tensile strength, low-temperature flexibility and toughness, are less than would be obtained from a linear low density polyethylene (LLDPE), due in part to the substantially non-linear nature of LDPE and the profusion of long-chain branches. Since LDPE is prepared under, for example, free-radical conditions and high pressures, it is highly branched. Highly branched polymers are polymers that have approximately one to two short chain branches for every one hundred carbon atoms in the polymer backbone. A short-chain branch is a branch of a polymer backbone of 6 carbon atoms or less which can be quantified by ¹³C NMR spectroscopic methods. See, for example, Randall, *Rev. Macromol. Chem. Phys.*, C29 (2 & 3), p. 285-297, incorporated herein by reference.

Conventional linear low density polyethylene (LLDPE) exhibits physical properties which are superior to that of LDPE at about the same range of resin densities, but show somewhat higher secant moduli and are difficult to process, resulting in foams with poor cell structure and higher than desired foam structure densities. LLDPE resins, produced by conventional Ziegler transition metal catalysts in the copolymerization of ethylene with one or more alpha-unsaturated monomers, can exhibit considerably narrower molecular weight distributions than LDPE, higher molecular weights, and typically only about 15-20 short-chain branches per 1000 carbon atoms. Commercially-available LLDPE resins with densities below about 0.910 g cm⁻³ are unavailable, thus further limit the flexibility of foam structures thereof.

Very low density polyethylene (VLDPE) is a special subset of LLDPE wherein an even greater number of "short-chain branches" (ca. 30-50 per 1000 carbon atoms) are effected by appropriate level of comonomer to result in much lower resin densities than LLDPE, e.g. 0.88 g cm⁻³ to 0.91 g cm⁻³. These materials thus exhibit greater flexibility than LLDPE. However, generally with conventional linear polyolefins, the greater the number of short-chain branches, the lower the resulting resin density, but also the shorter the length of the molecular backbone.

A single-site initiated polyolefin resin is a polyolefin prepared from a single-site initiator that has controlled molecular weights and molecular weight distributions. The polyolefin can be polyethylene or a copolymer of ethylene and alpha-unsaturated olefin monomers. One class of a single-site initiators of particular interest are the metallocene initiators which are described, for example, in J. M. Canich, U.S. Pat. No. 5,026,798, in J. Ewen, et al., U.S. Pat. No. 4,937,299, in J. Stevens, et al., U.S. Pat. No. 5,064,802, and in J. Stevens, et al., U.S. Pat. No. 5,132,380, each of which is incorporated herein by reference. These initiators, particularly those based on group 4 transition metals, such as zirconium, titanium, or hafnium, are high activity ethylene polymerization initiators.

A copolymer is a polymer resulting from the polymerization of two or more monomeric species and includes terpolymers (e.g., resulting from the polymerization of three monomeric species), sesquipolymers, and greater combinations of monomeric species.

The densities, or specific gravities, of the polymer resins can be measured using ASTM D-792 methods.

Maleic anhydride-grafting is covalently bonding one or more maleic anhydride groups to the original polymer chains. The grafting is generally accomplished by forming active grafting sites on the original polymer chain in the presence of maleic anhydride which can react to form a covalent bond between the polymer and the maleic anhydride. Active grafting sites can be generated, for example, by radicals or anions.

High vinyl acetate content EVA copolymers have vinyl acetate contents of greater than 8 percent, preferably greater than 17 percent and more preferably greater than 28 percent. High vinyl acetate content EVA copolymers generally produce undesirable foams that are mushy, sticky, have no tear strength, and exhibit excessive amounts of voiding and holes. Previous attempts to cross-link high vinyl acetate content ethylene-vinyl acetate copolymers have met with difficulty. The addition of a maleic anhydride grafted component to a mixture including an EVA allows the use of a high vinyl acetate content EVA in a product. The maleic anhydride permits the material to be cross-linked in a manner that reduces the tackiness and maintains the flexibility of the article in a foamed or non-foamed condition.

In particular, low density closed or open cell EVA foamed articles (e.g., high vinyl acetate content EVA foams) can be prepared and processed when maleic anhydride grafted components are included in the mixture that is cross-linked and expanded. Foams having high densities (over 20 pounds per cubic foot), medium densities (10 to 12 pounds per cubic foot), and low densities (1.5 to 2.0 pounds per cubic foot) can be prepared with these materials. The resultant foams are tough but soft materials that can be utilized as produced. Tough materials have a tensile strength greater than about 45 psi and a tear Die C greater than about 5 psi. Soft materials have a durometer Shore OO less than about 50 and a compression deflection less than about 5 psi, preferably less than 3.5 psi, and more preferably less than 3 psi. In addition to having low tackiness and good flexibility, the materials have a greater ability to be dipped (e.g., in a PVC dip coating process), coated, laminated to other materials, or bonded with an adhesive.

The foamed materials including maleic anhydride have several enhanced foam properties. Lower densities can be attained, less blocking and sticking of foam pieces can occur, compression recovery can be improved, resilience can be increased, and improved tensile, tear and elongation

properties can be observed. In addition, the foams can have a lower compression deflection than previously achievable without using plasticized materials. The foams have properties that are comparable to polyurethane foams, PVC foams, or elastomeric foams.

Maleic anhydride grafted materials containing EVA are more easily processed than materials that do not include maleic anhydride. The low tackiness of the maleic anhydride material allows continuous sheet production by horizontal and vertical foaming. In addition, additional melt strength can be imparted to the polymer compound which allows foaming to a higher density or to thicker gauges in vertical foaming processes.

Soft foams can shrink near the center of the foam, thereby forming a "dish" or a "sink," which results in a loss of usable material. Foams exhibiting little or no shrinkage near the center of the material reduce the amount of dishing or sinking that occurs. The addition of maleic anhydride to the materials can result in soft foams having thicknesses of five inches or greater with little or no dishing or sinking.

The maleic anhydride can improve the physical properties of foamed articles including components such as colorants or fillers. The maleic anhydride can reduce leaching of colorants or other additives from the material, for example, by increasing the amount of cross-linking in the material.

Other features and advantages of the invention will be apparent from the following detailed description thereof, and from the claims.

DETAILED DESCRIPTION

Polymer articles can be prepared from a mixture including an ethylene-vinyl acetate (EVA) copolymer and a maleic anhydride grafted component. A portion of the mixture is cross-linked. The mixture can be foamed.

The EVA copolymer can have a vinyl acetate content of between about 9 and 60 percent vinyl acetate. Preferably, the vinyl acetate content of the ethylene vinyl acetate copolymer is between 15 and 50 percent. Suitable EVA copolymers can have vinyl acetate (VA) contents of 9 percent, 17 percent, 23 percent, 28 percent, or 40 percent. Commercially available EVA copolymers include AT Polymers 1070C (9% VA), AT Polymers 1710 (17% VA), AT Polymers 2306 (23% VA), AT Polymers 2803 (28% VA), AT Polymers 2810 (28% VA), Chevron/Ace Plastics TD 3401 (9.5% VA), Chevron/Ace Plastics DS 4089-70 (18% VA), DuPont Elvax 40 (40% VA), DuPont Elvax 140-W (33% VA), DuPont Elvax 250-W (28% VA), DuPont Elvax 260 (28% VA), DuPont Elvax 350 (25% VA), DuPont Elvax 360 (25% VA), DuPont Elvax 450 (18% VA), DuPont Elvax 460 (18% VA), DuPont Elvax 550 (15% VA), DuPont Elvax 560 (15% VA), DuPont Elvax 650 (12% VA), DuPont Elvax 660 (12% VA), DuPont Elvax 750 (9% VA), DuPont Elvax 760 (9.3% VA), DuPont Elvax 770 (9.5% VA), Exxon Escorene LD-740 (24.5% VA), Exxon Escorene LD-724 (18% VA), Exxon Escorene LD-721.62 (19.3% VA), Exxon Escorene LD-721.88 (19.3% VA), Exxon Escorene LD-721 (19.3% VA), Exxon Escorene LD-740 (24.5% VA), Exxon Escorene LD-318 (9% VA), Exxon Escorene LD-319.92 (9% VA), Exxon Escorene LD-725, Quantum UE 630-000 (17% VA), Quantum 637-000 (9% VA), Rexene X1903 (10% VA), Rexene X0901 (12% VA), Rexene X0911 (18% VA), and Rexene X0915 (9% VA).

The mixture can include other components, such as polyolefinic polymers or resins, which can alter the physical properties of the article. The components of the mixture can be blended before or after grafting or cross-linking. The

polyolefinic polymer can include a low density polyethylene (LDPE), a very low density polyethylene (VLDPE), a linear low density polyethylene (LLDPE), a single site initiated polyethylene (e.g., PE, LDPE, or VLDPE), a polypropylene, a single-site initiated polypropylene, an ethylene-propylene diene monomer (EPDM) copolymer, an ethylene-propylene rubber (EPR), a single-site initiated ethylene-propylene diene monomer copolymer, a single-site initiated ethylene-propylene rubber, a high density polyethylene (HDPE), a polystyrene, a styrene copolymer, an ethylene-styrene interpolymer, a polyacrylonitrile, a polybutadiene, a polyvinylchloride (PVC), a polyvinylidene chloride, a polyvinylfluoride, a polyvinylidene fluoride, a polyvinyl acetate, a polyvinyl alcohol, a polyamide, a polyacrylate (e.g., a polymethyl acrylate or a polymethyl methacrylate), a polychlorotrifluoroethylene, a polytetrafluoroethylene, a cellulose, a polyester, a polyhalocarbon, and copolymers of ethylene with propylene, isobutene, butene, hexene, octene, vinyl chloride, vinyl propionate, vinyl isobutyrate, vinyl alcohol, allyl alcohol, allyl acetate, allyl acetone, allyl benzene, allyl ether, maleic anhydride, ethyl acrylate (EEA), methyl acrylate, acrylic acid, or methacrylic acid and blends or alloys thereof. Preferably, the polyolefinic polymer is a low density polyethylene, a very low density polyethylene, a linear low density polyethylene, a single-site initiated polyethylene, an ethylene-propylene diene monomer copolymer, an ethylene-propylene rubber, a single-site initiated ethylene-propylene diene monomer copolymer, or a single-site initiated ethylene-propylene rubber.

LDPE resins are described, for example, in "Petrothene Polyolefins . . . A Processing Guide," Fifth Edition, Quantum USI Division, 1986, pages 6-16, incorporated herein by reference. Some LDPE resins are commercially available from Exxon Chemical Company, Houston, Tex., Dow Plastics, Midland, Mich., Novacor Chemicals (Canada) Limited, Mississauga, Ontario, Canada, Mobil Polymers, Norwalk, Conn., Rexene Products Company, Dallas, Tex., Quantum Chemical Company, Cincinnati, Ohio, and Westlake Polymers Corporation, Houston, Tex. Commercially available LDPE resins include Eastman 1924P, Eastman 1550F, Eastman 800A, Exxon LD 117.08, Exxon LD 113.09, Dow 535I, Dow 683, Dow 760C, Dow 768I, Dow 537I, Novacor LF219A, Novacor LC05173, Novacor LC0522A, Mobil LMA-003, Mobil LFA-003, Rexene 2018 (7018), Rexene 1023, Rexene XO 875, Rexene PES050, Rexene PE1076, Rexene PE2030, Quantum NA953, Quantum NA951, Quantum NA285-003, Quantum NA271-009, Quantum NA324, Westlake EF606AA, Westlake EF612, and Westlake EF412AA. A commercially available VLDPE is Union Carbide 1085.

Some EPR and EPDM resins are available commercially from Exxon Chemical Company, Houston, Tex., under the tradename Vistalon™, and include Vistalon™ 5800, Vistalon™ 6205, Vistalon™ 7000, Vistalon™ 7500, Vistalon™ 8000, Vistalon™ 2200, Vistalon™ 2504, Vistalon™ 2555, Vistalon™ 2727, Vistalon™ 4608, Vistalon™ 719, Vistalon™ 3708, Vistalon™ 404, Vistalon™ 457, Vistalon™ 503, Vistalon™ 707, and Vistalon™ 878. Other EPDM resins are available commercially from DuPont, Wilmington, Del., under the tradename Nordel™, and include Nordel™ 2522, Nordel™ 2722, Nordel™ 1440, Nordel™ 1470, Nordel™ 1145, Nordel™ 1040, and Nordel™ 1070.

Single-site initiated polyolefin resins are described, for example, in S.-Y. Lai, et al., U.S. Pat. Nos. 5,272,236, 5,278,272, and 5,380,810, in L. Spenadel, et al., U.S. Pat. No. 5,246,783, in C. R. Davey, et al., U.S. Pat. No. 5,322,

728, in W. J. Hodgson, Jr., U.S. Pat. No. 5,206,075, and in F. C. Stehling, et al., WO 90/03414, each of which is incorporated herein by reference. Some single-site initiated polyolefin resins are available commercially from Exxon Chemical Company, Houston, Tex., under the tradename Exact™, and include Exact™ 3022, Exact™ 3024, Exact™ 3025, Exact™ 3027, Exact™ 3028, Exact™ 3031, Exact™ 3034, Exact™ 3035, Exact™ 3037, Exact™ 4003, Exact™ 4024, Exact™ 4041, Exact™ 4049, Exact™ 4050, Exact™ 4051, Exact™ 5008, and Exact™ 8002. Other single-site initiated resins are available commercially from Dow Plastics, Midland, Mich. (or DuPont/Dow), under the tradenames Engage™ and Affinity™, and include CL8001, CL8002, EG8100, EG8150, PL1840, PL1845 (or DuPont/Dow 8445), EG8200, EG8180, GF1550, KC8852, FW1650, PL1880, HF1030, PT1409, CL8003, Dow 8452, Dow 1030, Dow 8950, Dow 8190, and D8130 (or XU583-00-01).

A component of the mixture, such as a polyolefinic polymer or EVA, is grafted with maleic anhydride. Maleic anhydride-grafting of the polyolefinic polymer or polymer blend occurs when a polymer backbone is activated and reacts with maleic anhydride to form the graft. Levels of grafting can be adjusted by varying the amount of maleic anhydride introduced to the polyolefinic polymer or blend. The maleic anhydride-grafting can be carried out in a separate process, or in a continuous blending process.

Maleic anhydride grafting is generally accomplished in the presence of a graft initiator, such as an organic peroxide. Generally during grafting, the graft initiator is included with the maleic anhydride to perform a hydrogen abstraction from the polyolefin resin backbone which initiates grafting of the maleic anhydride to the polymer chain. Alternatively, maleic anhydride can be grafted to a polymer through gamma or ultraviolet irradiation in the presence of a photosensitizer. Grafting yields a polymer containing covalently bonded individual succinic anhydride units formed by the reaction of maleic anhydride with the polymer. Further side reactions can provide cross-linking. Maleic anhydride grafting is described, for example, in Gaylord, "Reactive Extrusion in the Preparation of Carboxyl-Containing Polymers and Their Utilization as Compatibilizing Agents" in *Reactive Extrusion: Principles and Practice*, M. Xanthos, Ed., Carl Hanser Verlag, 1992, Ch. 3, pg. 58, and in U.S. Pat. No. 4,927,888, each of which is incorporated herein by reference.

Maleic anhydride grafted materials can be prepared by reactive compounding of a material such as a polymer resin, maleic anhydride, and a grafting initiator. In general, maleic anhydride is blended with a grafting initiator which can be a peroxide such as dicumyl peroxide. Other suitable peroxides can be selected based on peroxide characteristics such as the decomposition half life at processing temperature and the residence time in the specific reaction process equipment.

The polymer, maleic anhydride and grafting initiator can be added to the feed section of an extruder, melted, mixed and pressurized. Maleic anhydride is a solid at room temperature, and melts to a low viscosity liquid at approximately 132° F. Melted maleic anhydride can be pumped to the reactor or the solid can be preblended with the polymer prior to introduction to the reactor. The reactor can be a screw extruder (e.g., a single screw or twin screw extruder). After grafting is complete, maleic anhydride which is unreacted is removed from the blend. This can be conveniently accomplished by venting the extruder to atmosphere, or, preferably, by using a vacuum, after the reaction has been completed, and prior to passing through the die.

The grafted mixture is then forced through a die forming a strand that can be cooled and chopped into pellets for the next step in the process. Alternatively, a die that immediately chops the strands into pellets upon exiting the die can be used.

Suitable maleic anhydride-grafted materials are also available commercially, for example, from Union Carbide Corporation, Exxon Chemical Company, DuPont Industrial Polymers, or Uniroyal Chemical. Suitable materials include: VLDPE grafted with about 0.9 weight percent maleic anhydride (MAH), such as Union Carbide DEFB 1373NT; VLDPE grafted with about 0.8 weight percent MAH, such as Union Carbide DEFB 1372NT; HDPE grafted materials, such as DuPont Fusabond E MB-100D (0.9% MAH) and Uniroyal Polybond 3009; LLDPE grafted with about 0.9% MAH, such as DuPont Fusabond E MB-226D; LLDPE grafted with about 0.65% MAH, such as DuPont Fusabond E BA-413D; ethylene propylene rubber grafted materials, such as DuPont Fusabond N MF-416D (0.9% MAH) and DuPont Fusabond N MF-418D (0.3% MAH); EPDM grafted materials, such as Exxon Exxelor VA 1801 (semicrystalline, 0.6% MAH graft), Exxon Exxelor VA 1803 (amorphous, 0.7% MAH graft), Exxon Exxelor VA 1810 (semicrystalline, 0.5% MAH graft), Exxon Exxelor VA 1820 (semicrystalline, 0.3% MAH graft), DuPont Fusabond N MF-274D (0.3% MAH), Uniroyal Chemical Royaltuf EDPM 490, and Uniroyal Chemical Royaltuf EDPM 485; polypropylene grafted materials, such as Exxon Exxelor PP1015 (0.4% MAH), DuPont Fusabond P MZ-109D (0.55% MAH), DuPont Fusabond P MZ-353D (1.4% MAH), Uniroyal Polybond 3150, and Uniroyal Polybond 3200; ethylene acrylate terpolymer grafted with about 0.85% MAH, such as DuPont Fusabond A MG-423D; and ethylene vinyl acetate grafted with about 0.8% MAH, such as DuPont Fusabond C MC-190D (28% VA) and DuPont Fusabond C MC-197D (18% VA). The commercial materials can be incorporated into the mixture as substitutes for or in combination with the reactive-compounded materials described above.

The grafted component can include other grafted monomers, such as di- and tri-allyl cyanurates and isocyanurates, alkyl di- and tri-acrylates and methacrylates, zinc dimethacrylates and diacrylates, styrenes, and butadiene.

The maleic anhydride grafted component is blended with EVA and cross-linking agents to form a mixture. Methods of combining the components of the foamable mixture include, for example, melt-blending, diffusion-limited imbibition, or liquid mixing. Any or all of the ingredients can be pulverized or reduced in particle-size by other methods prior to use. Blending can be accomplished by dry blending pellets of the individual components either by batch processes or as a continuous feed processes to an extruder. The components can be mixed, for example, in an internal mixer such as a Banbury mixer, a single or twin screw extruder, or any other mixer capable of providing sufficient heating for melting and fluxing for complete and uniform mixing of the materials (i.e., a laboratory two roll mill). It is preferred that the blending be carried out with temperature control. The blending or mixing provides a uniform mixture. Components can be introduced to the mixture sequentially at any step during the mixing operation. Once mixed, the hot foamable compounded mixture is sheeted, for example, through a two roll mill.

Other resins, foaming agents, and other additives can be included in the mixture. Other additives that can be added to the foam compositions include particulate and fibrous fillers

to reinforce, strengthen or modify the rheological properties of the foam composition, antioxidants (e.g., hindered phenolics such as Irganox 1010 or Bennox 1010, phosphites such as Irgafos 168, or polymerized trimethyldihydroquinoline such as Agerite AK, Resin D or Flectol H), ultraviolet stabilizers, thermal stabilizers, antistatic components, flame retardants, pigments, colorants, and other processing aids.

Foaming agents can be included in the mixture to produce foamed articles. The expanding medium, or foaming agent, can include a physical foaming agent or a chemical foaming agent. A physical foaming agent is a medium expanding composition that is a gas at temperatures and pressures encountered during the foam expanding step. Typically, a physical foaming agent is introduced to the polymer blend in the gaseous or liquid state and expands, for example, upon a rapid decrease in pressure.

Physical foaming agents include low molecular weight organic compounds including C_1 - C_6 hydrocarbons such as acetylene, propane, propene, butane, butene, butadiene, isobutane, isobutylene, cyclobutane, cyclopropane, ethane, methane, ethene, pentane, pentene, cyclopentane, pentene, pentadiene, hexane, cyclohexane, hexene, and hexadiene, C_1 - C_5 organohalogens, C_1 - C_6 alcohols, C_1 - C_6 ethers, C_1 - C_5 esters, C_1 - C_5 amines, ammonia, nitrogen, carbon dioxide, neon, or helium. The preferred foaming agents include butane, isobutane, carbon dioxide, and 1,1-difluoroethane (HFC-152a). The preferred physical foaming agent concentration prior to expanding the foam is between 0.5 and 30 percent.

A chemical foaming agent is compound or mixture of compounds that decomposes at elevated temperatures to form one or more gasses, which can be used to expand the compositions into a foam. In general, the chemical foaming agent will have a decomposition temperature (with the resulting liberation of gaseous material) from 130° C. to 350° C. Examples of chemical foaming agents include azodicarbonamide, p,p'-oxybis(benzene)sulfonyl hydrazide, p-toluene sulfonyl hydrazide, p-toluene sulfonyl semicarbazide, 5-phenyltetrazole, ethyl-5-phenyltetrazole, dinitroso pentamethylenetetramine, and other azo, N-nitroso, carbonate and sulfonyl hydrazides. In addition, various acid/bicarbonate mixtures decompose into gasses when heated. The preferred chemical foaming agent concentration prior to expanding the foam is between 2 and 30 percent.

Cross-linking of the mixture can aid in the formation of desirable foamed and non-foamed materials. Cross-linking can also lead to improvements of the ultimate physical properties of the materials, such as flexibility and low tackiness. Cross-linking can take place prior to, during, or after expansion of the foam.

One method of cross-linking is by reaction with a peroxide. Cross-linking can also be accomplished by grafting vinyl silane groups onto a component of the mixture and activating cross-linking by exposing the mixture to moisture. Silane cross-linking can be useful for making thin gauged foamed articles such as tape grade foams. A combination of peroxide and silane cross-linking can also be used. In the case of peroxide, the cross-linking can be accomplished in the beginning zones of a foaming chamber via heat activation or in another heat treatment process. Silane cross-linking can be activated by exposure to a source of moisture, for example, prior to expansion in an oven.

When cross-linking with a peroxide, heating the peroxide causes it to generate radicals which react with the compo-

nents of the mixture to cause covalent cross-links in the mixture. By regulating the amounts and types of organic peroxide present in the mixture, the relative rates of radical generation, abstraction, and cross-linking steps can be controlled to permit foaming of the polymer materials. The resulting materials have high cross-link levels. Peroxide cross-linking is described in detail in Park, *Handbook of Polymeric Foam and Foam Technology*, "Polyolefin Foam," Ch. 9, pp. 186-242, which is incorporated herein by reference.

Hydrolyzable silanes can be grafted to a component of the mixture to make the mixture cross-linkable by exposure to moisture. Silane-grafted materials are formed by grafting a material such as a polyolefinic polymer to an azido- or vinyl-functional silanes having the general formula $RR'SiY_2$, in which R represents an azido- or vinyl-functional radical attached to silicon through a silicon-carbon bond (e.g., composed of carbon, hydrogen, and optionally sulfur, nitrogen and oxygen), each Y represents a hydrolyzable organic radical (e.g., a radical that can be cleaved from silicon by the addition of water); and R' represents a monovalent hydrocarbon radical or a hydrolyzable organic radical. Suitable vinyl-functional silanes include vinyl-functional alkoxy silanes such as vinyl trimethoxy silane (VTMOS) and vinyl triethoxy silane (VTEOS). Silane grafting is described, for example, in U.S. Ser. No. 08/872,736, filed Jun. 11, 1997, U.S. Pat. No. 5,859,076 which is incorporated herein by reference.

The mixture can also be cross-linked with high-energy, ionizing radiation involve the use of equipment which generates electrons, X-rays, Beta-rays or Gamma-rays. The most preferred method for cross-linking olefinic compositions through exposure to ionizing radiation is through the use of an electron-beam radiation source. Exposure of the compositions of the present invention to ionizing radiation may be accomplished at dosages in the range of about 0.1 to 40 Megarads, and preferably, at about 1 to 20 Megarads. U.S. Pat. No. 4,203,815 (Noda) discloses methods of exposing compositions to both high and low-energy ionizing radiation to effect improvements in surface quality, strength and subsequent heat-sealing or embossing processes. The amount of cross-linking may be appropriately controlled by the dosage of ionizing radiation.

Regardless of the method of cross-linking used, acceptable foam articles can only be obtained in certain ranges of cross-linking density or level, which is related to the amount of grafting in the blend. Too much cross-linking prior to foaming can render the foam inelastic, resulting in less than optimal expansion and greater than optimal density for a given level of foaming agent. Too little cross-linking can be detrimental to physical properties such as compression set properties or thermal resistance, for example. It is important to choose cross-linking levels that afford foams with particular desired properties. Grafting with maleic anhydride and cross-linking can increase the melt strength of the composition. The cross-linking levels can be determined by establishing the gel content of the of the composition, for example, by extraction with a solvent such as xylenes. The gel content of the foams are preferably in the range of about 10 to about 95 percent, and preferably in the range of about 25 to about 90 percent.

The graft initiator or cross-linking agent can be a radical generating species, for example, a peroxide. Examples of peroxides include dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di-(t-butylperoxy)cyclohexane, 2,2'-bis(t-butylperoxy)diisopropylbenzene, 4,4'-bis(t-

butylperoxy)butylvalerate, t-butylperbenzoate, t-butylperterephthalate, and t-butyl peroxide. Most preferably, the graft initiator is dicumyl peroxide, such as 40% active dicumyl peroxide (e.g., Luperco 500 40KE).

In a continuous production process, the process steps can be categorized as reactive compounding, blending, extrusion, and cross-linking. The material from the blending step can be extruded using a conventional plastic sheet extrusion line into a prefoamed and uncross-linked sheet. This is accomplished by pumping the melted mixture through a sheet die on the end of the extruder, and passing the extruded sheet through cooling and polishing rolls. The product forms a continuous sheet which is collected in roll form. The maleic anhydride can facilitate cross-linking and handling of the foam material in the solid sheet form.

The article can be cross-linked and/or expanded in a continuous process or a compression molding (e.g., batch) process.

In the continuous process, expansion to form a foam takes place in a foaming chamber of a continuous oven. For example, an extruded sheet can enter a heated chamber of the oven, normally supported on a mesh belt in a horizontal oven or suspended vertically in a vertical oven. The material is heated above the decomposition temperature of the chemical foaming agent contained in the mixture, thereby expanding the material into a foam which exits the oven as a continuous sheet. This process can be used to produce continuous sheets of foam incorporating a high level of EVA resin, for example, up to 40% vinyl acetate. A product containing a 40% vinyl acetate EVA copolymer would normally be too tacky to handle and too soft to convey through the process (i.e., it tends to stick to the belt). The addition of the maleic anhydride can enhance the effects of cross-linking, reduce the tackiness, and improve the strength of the material so that it can be more easily handled and conveyed throughout the process.

In a compression molding (e.g., batch) process, the sheet can be cut, for example, into the a rectangular shaped preform to fill a mold prior to foaming in a mold cavity. The preform is inserted into a the mold cavity in a preheated hydraulic press. More than one mold can be included in the hydraulic press. Once loaded, the hydraulic press is closed. The filled mold is held in the hydraulic press for predetermined press cycle time to begin the cross-linking and expanding process. The time, temperature, and clamping pressure can be modified to afford foams having optimized properties.

Following the completion of the hydraulic pressing cycle, the press is released and the partially cured and expanded material is removed from the press. The partially cured and expanded material is then transported in the mold to a pre-heated secondary expansion press for a second predetermined press cycle (i.e., time, temperature, and clamping pressure that have previously been determined to optimize foam properties) to complete the cross-linking and expansion of the material.

Once the expanding and cross-linking processes are complete, or nearly complete, the foam block (e.g., bun) can be cooled and removed from the secondary expansion press and the mold cavity. Once cooled, the foam block can be washed and allowed to dry.

After cross-linking and expanding the mixture including EVA and maleic anhydride grafted to a component of the mixture, the foam can contain open cells, closed cells, or a combination thereof. The closed cells can be converted to open cells by crushing the foam and allowing the material to recover. The formulation of the foam gives the material the physical properties necessary for recovery. The foam can be crushed manually, mechanically (e.g., with a press), or with a cell crushing apparatus that permits fast material throughput. The crushing device can include a pinning device that punctures closed cells. Pinning can take place before, during, or after crushing. After crushing, the open cell foam can have greater than 50 percent open cells (e.g., up to 98 percent). Conversion of closed cells to open cells is described in more detail, for example, in U.S. Ser. No. 08/872,736, incorporated herein by reference.

Maleic anhydride grafted materials can be used in molding processes to expand a particular form in mold from a mixture containing foaming agents. The non-foamed materials included a maleic-anhydride component can be in the shape of, for example, pellets, granules, chips, powder, fragments, or other small particulates which can enter small crevice areas of a mold. In this process, the expanding and cross-linking step can take place completely in the mold. Alternatively, the molding process can occur in two independent cross-linking and expanding steps. The mixture has sufficient time to flow and foam in difficult to fill cracks and crevices without being so cross-linked as to prevent material flow. The molding process can be used to mold products such as, for example, automotive bumpers, packaging, or footwear from the maleic anhydride grafted materials.

The maleic anhydride grafted materials can be used in injection molding, compression molding, transfer molding, rotational molding, slush molding, injection molding, thermoforming and/or laminating molding, or other types of molding operations. The maleic anhydride grafted materials can also be used to form sheets, including thin, tape grade rolls. Tape grade foams can have thicknesses between about 0.015 and $\frac{1}{8}$ inch and densities between about 1.5 and 40 pounds per cubic foot. In addition, the maleic anhydride grafted materials can be used to manufacture of solid sheet materials, cast films, extruded films, extruded coatings, wire and cable, and profile extrusions. In each of these applications, the maleic anhydride grafted materials can be foamed or non-foamed.

The high vinyl acetate content allows the foams to be used in applications which require dipping, coating, lamination, or bonding to adhesives. Dip materials are described, for example, in U.S. Pat. No. 5,021,290.

Maleic anhydride grafting can increase the strength of the foamed article, permitting the use of the foam in applications that require an increase in tensile strength and tear resistance, such as packaging, cushioning, and shock attenuating applications. The open cell foams have good flexibility at low temperatures; the foams can provide cushioning over a broad range of temperatures (i.e., between -90° F. and 200° F.). The foams can be used, for example, in situations where ease in skiving is necessary, such as in producing flotation vests or cushions.

The foams can also be used where a soft foam of greater thickness is required, as the foams can be as large as 10

inches thick (e.g., 2 to 4 inches thick). The softness of the material can be modified by blending other polymers into the mixture before expanding to form a foam while maintaining the strength of the material. Similarly, the foam density can also be varied by adjusting the amount and conditions of the cross-linking and expansion steps.

The following specific examples are to be construed as merely illustrative, and not limitative, of the remainder of the disclosure.

EXAMPLE 1

A foamed article including EVA and maleic anhydride was produced in a compression molding process. A VLDPE resin was grafted with maleic anhydride (MAH) and compounded with other ingredients to give a mixture having the following formulation:

Formulation Component	Example 1 Parts per hundred resin (PHR)
VLDPE (grafted with 0.9% MAH)	10
EVA (28% VA content)	90
Zinc Oxide	0.13
Azodicarbonamide	14
Dicumyl Peroxide 40%	1.875
Antioxidant	0.2

The grafted polyolefinic resin and EVA were compounded with additional ingredients, including a blowing agent, activators, and an organic peroxide cross-linking agent as indicated in the above formulation. All ingredients were mixed on a two roll mill set at approximately 250° F. Mixing was accomplished by sequential addition of portions of the materials into the polymer. The fluxed and fused mixture was banded on the heated mill roll surface as is customary in mixing in this operation. Alternatively, the components can be mixed using an internal high intensity batch mixer. At the completion of the mixing operation, the hot compounded material was sheeted off the mill at approximately 3/8 inch thickness.

Multiple sheets were plied up (i.e., layered) into a pre-form for molding in a 1.25 inch×6 inch×6 inch high pressure hydraulic press mold while still hot. The mold containing the hot compound was put between heated high pressure hydraulic press platens under pressure for 50 minutes at 295° F. at 1000 psi. The mold was released and the resulting material was removed from the hydraulic press mold and inserted into a lower pressure mold cavity (i.e., at atmospheric pressure) of the expected final dimensions of 3 inches by 18 inches by 24 inches. The material was allowed to complete cross-linking and expansion in the lower pressure mold cavity for about 30 minutes at 330° F. The mold cavity and foamed material therein was cooled with water to room temperature. The expanded material was removed from the mold, yielding a closed cell foam having the physical properties summarized in Table I.

TABLE I

Property	Example 1
Density (pcf)	2.04
Tensile (psi)	50.8
Elongation (%)	431
25% Compression Deflection (psi)	3.26
50% Compression Deflection (psi)	9.77
50% Compression Set (%) (ASTM-3575)	25
50% Compression Set (%) (ASTM-1056)	48
Tear Die C (pli)	5.8
Durometer Shore A	0
Durometer Shore C	0
Durometer Shore 00	30
Durometer Shore FWC	8
Cell size average (mm)	0.20
Cell size min. (mm)	0.05
Cell size max. (mm)	0.40

EXAMPLE 2

The method described in Example 1 was used to prepare a foamed article having the following formulation:

Formulation Component	Example 2 Parts per hundred resin (PHR)
VLDPE (grafted with 0.9% MAH)	20
EVA (28% VA content)	80
Zinc Oxide	0.2
Azodicarbonamide	14
Dicumyl Peroxide 40%	1.75
Antioxidant	0.2

The resulting closed cell foam had a density of 2.34 pounds per cubic foot and a durometer Shore 00 of 36.

EXAMPLE 3

The method described in Example 1 was used to prepare a foamed article having the following formulation:

Formulation Component	Example 3 Parts per hundred resin (PHR)
VLDPE (grafted with 0.9% MAH)	30
EVA (28% VA content)	70
Zinc Oxide	0.2
Azodicarbonamide	14
Dicumyl Peroxide 40%	1
Antioxidant	0.2

The resulting foam was a closed cell foam.

EXAMPLE 4

The method described in Example 1 was used to prepare foamed articles having the following formulations:

	Example 4A	Example 4B	Example 4C
EVA (28% VA content)	60		80
EVA (23% VA content)		80	
EVA (17% VA content)	30		

-continued

	Example 4A	Example 4B	Example 4C
EVA (40% VA content)			15
EPDM	10	10	
VLDPE (grafted with 0.8% MAH)			5
Single-site initiated VLDPE		10	
Azodicarbonamide	15	14	20
Zinc oxide	0.05	0.05	0.13
dicumyl peroxide	1	1	1.2
antioxidant		0.1	0.3
clay		10	

The high pressure mold had dimensions of 1.25 inch×6 inch×6 inch. The mold containing the hot compound was put between heated high pressure hydraulic press platens under pressure for 45 minutes at 295° F. at 500 psi. The mold was released and the resulting material was removed from the hydraulic press mold and inserted into a lower pressure mold cavity (i.e., oven). The material was allowed to complete cross-linking and expansion in the lower pressure mold cavity for about 30 minutes at 330° F. The mold cavity and foamed material therein was cooled with water to room temperature.

A dip test procedure was performed on each of the samples. A foam sheet was skived to a thickness of one inch. The one inch thick foam sheet was cut into strips having a width of two inches and a length of twelve inches. A polyvinylchloride (PVC) dip solution was prepared from an acceptable base source, such as Flexibar 821-4019 solvent vinyl scarlet base, available from Flexibar Corporation. The base was mixed until uniform dip solution was formed. The dip solution was maintained at 70±3° F. at a relative humidity of 50 percent and atmospheric pressure.

Each foam strip was held vertically above the dip solution. The lower end of the foam strip was immersed approximately four inches into the dip. The foam strip was removed from the dip solution immediately after placing it in the dip. The dipped foam strip was held over the container of dip solution to permit the excess material to drip off. The wet dipped foam strip was placed on a surface in a manner to avoid contacting the dip layer portion of the foam strip. The dip layer was allowed to air dry for about one hour. The

dried single layer coated foam strip was dipped a second time following the same procedure. The double dipped foam strip was allowed to air dry for twenty four hours.

The quality of the dip layer was probed using two peel tests. In the cut and peel test, a knife blade was used to slit the dried dipped area, the dip layer was peeled back at knife cut, and the foam was examined for tears in the foam and/or for ease of peeling. In the rub and peel test, a section of the dip layer was rubbed with a thumb for about thirty seconds, the rubbed area (or blister if a blister formed) was peeled back, and the foam was examined for tears in the foam and/or for ease of peeling.

The resulting closed cell foam had the physical properties summarized in Table II.

TABLE II

	Example 4A	Example 4B	Example 4C
Density	2.08	2.29	1.44
Tensile	47	53.84	45
Elongation	452	367	337
25% Compression	2.4	2.9	2.49
Deflection			
50% Compression	7.95	8.75	8.59
Deflection			
50% Compression	28.78	32.8	30.12
Set			
Tear Die "C"	6.7	7.96	4.92
Split tear	4.65	4.93	
Shore A Durometer	0	0	0
Shore C Durometer	0	0	0
Shore 00 Durometer	18	22	25
Cell size mode mm	0.2	0.2	0.2
Cell size min. mm	0.05	0.05	0.05
Cell size max. mm	0.4	0.4	0.4
Appearance	few small voids in foam	some voids in foam	fine celled nice foam
PVC dip	sticks but can peel off	sticks but can peel off	better bond dip to foam

EXAMPLE 5

The method described in Example 1 was used to prepare a foamed articles having the following formulations:

	Example 5A	Example 5B	Example 5C	Example 5D
EVA (28% VA content)				10
EVA (18% VA content)		80		
EPDM (grafted with 0.7% MAH)		20	10	
EPDM (Uniroyal Chemical Royaltuf EDPM 490, grafted with MAH)			10	
EPDM	50			
VLDPE (grafted with 0.9% MAH)	10			
Single site initiated VLDPE	40		90	80
Zinc Stearate			0.3	
Azodicarbonamide	14	14	14	14
p,p'-oxybis(benzenesulfonyl				

-continued

	Example 5A	Example 5B	Example 5C	Example 5D
hydrazide)		0.1		0.1
Zinc oxide	0.13	0.2		0.2
dicumyl peroxide 40%	1	1.75	2.25	1.75
antioxidant	0.3	0.2		0.2

The high pressure mold had dimensions of 1.25 inch×6 inch×6 inch. The mold containing the hot compound was put between heated high pressure hydraulic press platens under pressure for 50 minutes at 295° F. at 1960 psi (60 minutes at 900 psi for Example 5A). The mold was released and the resulting material was removed from the hydraulic press mold and inserted into a lower pressure mold cavity (i.e., oven). The material was allowed to complete cross-linking and expansion in the lower pressure mold cavity for about 30 minutes at 330° F. The mold cavity and foamed material therein was cooled with water to room temperature. The materials were tested by PVC dip coating as described in Example 4.

The resulting foam had the physical properties summarized in Table III.

TABLE III

	Example 5A	Example 5B	Example 5C	Example 5D
Density (pcf)	1.90	2.08	2.33	2.04
25% Compression	1.9			
Deflection				
50% Compression	7.4			
Deflection				
50% Compression	30			
Set				
Tear Die "C"	5.05			
Shore 00	20	32	42	38
Durometer				
Cell size mode mm	0.3			
Cell size min. mm	0.05			
Cell size max. mm	0.6			
Appearance	nice foam	nice foam	satisfactory foam, had some voids	satisfactory foam
PVC dip	improved dip bond	improved dip bond	satisfactory dip	satisfactory dip

EXAMPLE 6

Four EVA copolymers having different vinyl acetate contents were used to formulate Example 6A (9% vinyl acetate), Example 6B (17% vinyl acetate), Example 6C (23% vinyl acetate), and Example 6D (28% vinyl acetate). The samples had the following general formulation.

Component	Weight percent (%)
EVA copolymer	56.3
VLDPE (grafted with 0.8% MAH)	13
Foaming Agent Compound	29.3
Dicumyl Peroxide Compound	1.3

The foaming agent compound was 40 percent azodicarbanonamide in 60 percent EVA copolymer. In Examples 6A

and 6B, the foaming agent was compounded with a 9% vinyl acetate EVA copolymer. In Examples 6C and 6D, the foaming agent was compounded with a 23% vinyl acetate EVA copolymer. The dicumyl peroxide compound was 60% dicumyl peroxide dispersed in an acrylic polymer.

For each example, the materials were dry blended and extruded in a single screw extruder to form a rod having a diameter of about 0.5 inches. The rod was cut to pieces having lengths of approximately four inches. The rods were placed in a circulating hot air oven at a temperature of 450° F. The rods were left in the oven until they fully expanded, as observed visually through an oven window.

Each of Examples 6A–6D produced foams having uniform fine cells. The foams were less tacky and had more hot strength than equivalent foams produced using peroxide

cross-linking without containing maleic anhydride. The reduced tackiness and increase hot strength of the foams including maleic anhydride indicates that foams that are normally difficult to handle in a conventional horizontal foaming oven due to sticking to a conveyor belt and structural weakness can be processed effectively by including maleic anhydride.

EXAMPLE 7

Samples having the following formulations were prepared.

Component	Example 7A	Example 7B	Example 7C
Weight percent (%)			
Silane grafted EVA Copolymer (9% VA)	61.5	67.5	57.5
Catalyst Compound	3.5	3.5	3.5
Foaming Agent Compound	15.5	15.5	15.5
EVA resin (23% VA)	11.0		
ULDPE (grafted with 0.8% MAH)		5.0	5.0
Activator Compound	6.0	6.0	6.0
White Color Concentrate	2.5	2.5	2.5

Example 7A was a control sample that did not contain maleic anhydride. The EVA resin added to Example 7A had a VA content from 5% to 50% to regulate overall VA level in the product.

The silane grafted EVA copolymer was prepared by grafting Exxon LD319 (9% VA content) with 0.37 percent vinyl trimethoxysilane (VTMOS) using dicumyl peroxide as the grafting initiator (20:1 VTMOS:dicumyl peroxide). The catalyst compound was 1.2 percent dibutyltin dilaurate in LDPE. The catalyst compound included 1 percent of a phenolic antioxidant (Irganox 1010). The foaming agent compound was 40 percent azodicarbonamide in LDPE. The activator compound was 30 percent zinc salt (10 percent zinc oxide and 20 percent zinc stearate) in LDPE. The white color concentrate was 50 percent TiO₂ in LDPE.

The formulation was dry blended and extruded into a sheet using a 2.5 inch extruder. The resultant sheet had a thickness of between 0.025 to 0.027 inches and a width of 8.1 inches. The extrusion temperature was maintained below 280° F. to avoid prefoaming of the sheet as it exits the die.

The extruded sheet was cross-linked by exposure to moisture in a condensing atmosphere at 150° F. wet bulb temperature for a period of 16 hours. The cross-linked sheet was foamed by passing through a chamber where it was exposed on both surfaces to a combination of infrared and hot air heating. The temperature of the sheet was raised to about 450° F., which activated the foaming agent and caused the material to expand.

The properties of the foams are summarized in Table IV.

TABLE IV

	Example 7A	Example 7B	Example 7C
Density (pcf)	4.8	5.1	4.8
50% Compression Set	20	18	20
Cell size mode (mm)	0.2	0.2	0.3

The foamed articles can also be produced by crosslinking the extruded sheet with radiation from sources including electron beam with absorbed doses between about 0.1 and 50 MRAD, preferably between about 1 and 8 MRAD.

The thin foamed articles of Example 7 can be useful in adhesive coating where the additional polarity of the maleic anhydride can improve bonding of the foam to the adhesive.

EXAMPLE 8

The non-foamed articles were prepared having the following formulations:

	Example 8A	Example 8B	Example 8C
ULDPE	5		5
ULDPE (grafted with 0.9% MAH)			
EVA (40% VA content)	15	15	15
EVA (28% VA content)	80	80	80
Dicumyl peroxide 40%	3	3	3
Antioxidant	0.3	0.3	0.3

The materials were compounded under laboratory conditions using a laboratory scale two roll open mill at a temperature of about 250° F. The compounded material was removed from the mill as 0.25 inch thick square sheets (6 inches by 6 inches). The minimum torque of mixing for Example 8A was 686, for Example 8B was 665, and for Example 8C was 656.

While the material was hot, it was placed in to a preheated high pressure mold cavity having dimensions of 0.25 inchx6 inchx6 inch. The mold containing the hot compound was put between heated high pressure hydraulic press platens under pressure for 30 minutes at 295° F. at 900 psi. The mold was released and the resulting material was removed from the hydraulic press mold. The material was cooled to room temperature in air.

Each formulation of Example 8 yielded a translucent, solid cross-linked sheet. The material of Example 8A was slightly tacky and had a Durometer A of 76. The material of Example 8B was slightly tacky and had a Durometer A of 72. The material of Example 8C, which included a maleic anhydride grafted component, was not tacky, was easy to process (e.g., milling produced the lowest torque). The material of Example 8C was softer than that of Example 8A or Example 8B, having a Durometer A of 69.

Other embodiments are within the claims.

What is claimed is:

1. A method of making a non-foamed polymer article comprising:

providing a mixture including maleic anhydride and an ethylene-vinyl acetate copolymer having a vinyl acetate content between about 9 and about 60 percent, the maleic anhydride being grafted to a portion of the mixture; and

cross-linking the mixture sufficiently to form a flexible article having low tackiness.

2. The method of claim 1, wherein the mixture further comprises a polyolefinic polymer.

3. The method of claim 2, wherein the polyolefinic polymer is grafted with maleic anhydride.

4. The method of claim 2, further comprising grafting maleic anhydride to the polyolefinic polymer.

5. The method of claim 2, wherein the polyolefinic polymer is selected from the group consisting of a low density polyethylene, a very low density polyethylene, a linear low density polyethylene, a single-site initiated polyethylene, an ethylene-propylene diene monomer copolymer, an ethylene-propylene rubber, a single-site ini-

tiated ethylene-propylene diene monomer, and a single-site initiated ethylene-propylene rubber.

6. The method of claim 1, wherein the ethylene-vinyl acetate copolymer is grafted with maleic anhydride.

7. The method of claim 1, further comprising grafting maleic anhydride to the ethylene-vinyl acetate copolymer.

8. The method of claim 1, wherein cross-linking includes cross-linking with a peroxide.

9. The method of claim 8, wherein the peroxide is dicumyl peroxide.

10. The method of claim 1, wherein cross-linking includes cross-linking with a silane.

11. The method of claim 1, wherein cross-linking includes cross-linking with radiation.

12. The method of claim 1, further comprising applying a coating, an adhesive, or a laminated layer to a surface of the article.

13. The method of claim 1, further comprising dipping the article to form a layer on a surface of the article.

14. A non-foamed article comprising a mixture including an ethylene-vinyl acetate copolymer having a vinyl acetate content between about 9 and about 60 percent, and maleic anhydride grafted to a component of the mixture, wherein the mixture is cross-linked sufficiently to provide a flexible article having low tackiness.

15. The non-foamed article of claim 14, wherein the vinyl acetate content of the ethylene-vinyl acetate copolymer is between about 9 and about 60 percent.

16. The non-foamed article of claim 14, wherein the mixture further comprises a polyolefinic polymer.

17. The non-foamed article of claim 16, wherein the polyolefinic polymer is grafted with maleic anhydride.

18. The non-foamed article of claim 17, wherein the article includes between about 1 and about 90 weight percent of the maleic anhydride grafted polyolefinic polymer.

19. The non-foamed article of claim 17, wherein the article includes between about 5 and about 30 weight percent of the maleic anhydride grafted polyolefinic polymer.

20. The non-foamed article of claim 17, wherein the maleic anhydride content of the grafted polyolefinic polymer is between about 0.01 and about 10 weight percent.

21. The non-foamed article of claim 17, wherein the maleic anhydride content of the grafted polyolefinic polymer is between about 0.5 and about 2.0 weight percent.

22. The non-foamed article of claim 14, wherein the vinyl acetate content of the ethylene-vinyl acetate copolymer is between about 15 and about 50 percent.

23. The non-foamed article of claim 14, wherein the portion of the mixture is cross-linked by a peroxide.

24. The non-foamed article of claim 14, wherein the portion of the mixture is cross-linked by a silane.

25. The non-foamed article of claim 14, wherein cross-linking includes cross-linking with radiation.

26. The non-foamed article of claim 14, wherein the article further comprises a surface having a layer formed by dipping.

27. The non-foamed article of claim 14, wherein the article further comprises a surface having a coating, a laminated layer, or an adhesive.

28. The non-foamed article of claim 16, wherein the polyolefinic polymer is selected from the group consisting of a low density polyethylene, a very low density polyethylene, a linear low density polyethylene, a single-site initiated polyethylene, an ethylene-propylene diene monomer copolymer, an ethylene-propylene rubber, a single-site initiated ethylene-propylene diene monomer copolymer, and a single-site initiated ethylene-propylene rubber.

29. The non-foamed article of claim 14, wherein the ethylene-vinyl acetate copolymer is grafted with maleic anhydride.

30. A non-foamed article comprising a mixture including an ethylene-vinyl acetate copolymer having a vinyl acetate content between about 9 and about 60 percent, and a maleic anhydride grafted polyolefinic polymer, wherein the mixture is cross-linked sufficiently to provide a flexible article having low tackiness.

31. The article of claim 30, wherein the vinyl acetate content of the ethylene-vinyl acetate copolymer is between about 9 and about 60 percent.

32. The article of claim 30, wherein the vinyl acetate content of the ethylene-vinyl acetate copolymer is between about 15 and about 50 percent.

33. The article of claim 30, wherein the article includes between about 1 and about 90 weight percent of the maleic anhydride grafted polyolefinic polymer.

34. The article of claim 30, wherein the article includes between about 5 and about 30 weight percent of the maleic anhydride grafted polyolefinic polymer.

35. The article of claim 30, wherein the maleic anhydride content of the grafted polyolefinic polymer is between about 0.01 and about 10 weight percent.

36. The article of claim 30, wherein the maleic anhydride content of the grafted polyolefinic polymer is between about 0.5 and about 2.0 weight percent.

37. The article of claim 30, wherein the portion of the mixture is cross-linked by a peroxide.

38. The article of claim 30, wherein the portion of the mixture is cross-linked by a silane.

39. The article of claim 30, wherein cross-linking includes cross-linking with radiation.

40. The article of claim 30, wherein the article further comprises a surface having a layer formed by dipping.

41. The article of claim 30, wherein the article further comprises a surface having a coating, a laminated layer, or an adhesive.

42. The article of claim 30, wherein the polyolefinic polymer is selected from the group consisting of a low density polyethylene, a very low density polyethylene, a linear low density polyethylene, a single-site initiated polyethylene, an ethylene-propylene diene monomer copolymer, an ethylene-propylene rubber, a single-site initiated ethylene-propylene diene monomer copolymer, and a single-site initiated ethylene-propylene rubber.

43. The article of claim 30, wherein the ethylene-vinyl acetate copolymer is grafted with maleic anhydride.

44. The article of claim 30, wherein the mixture is foamable.

EXHIBIT F

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Andersen et al.

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3

(54) **THERMOPLASTIC STARCH
COMPOSITIONS INCORPORATING A
PARTICULATE FILLER COMPONENT**

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(57) **ABSTRACT**

Thermoplastic starch compositions that include a particulate filler, e.g. an inorganic filler component, and optional fibrous component. The compositions include a thermoplastic phase comprising a thermoplastic starch melt that contains, at a minimum, starch blended with an appropriate plasticizing agent under conditions in order for the starch to form a thermoplastic melt. The thermoplastic phase may also include one or more additional thermoplastic polymers and other optional reactants, liquids or cross-linking agents to improve the water-resistance, strength, and/or other mechanical properties of the thermoplastic melt, particularly upon solidification. The inorganic filler component may affect the mechanical properties but will mainly be added to reduce the cost of the thermoplastic starch compositions by displacing a significant portion of the more expensive starch or starch/polymer melt. Fibers may optionally be included in order to improve the mechanical properties of the thermoplastic starch compositions. The thermoplastic starch compositions may be shaped into a wide variety of useful articles, such as sheets, films, containers, and packaging materials. Because the thermoplastic starch compositions will typically include a thermoplastic phase that is biodegradable, and because the other components will either constitute a naturally occurring mineral and optionally a natural fiber, the overall composition will typically be more environmentally friendly compared to conventional thermoplastic materials.

96 Claims, No Drawings

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THERMOPLASTIC STARCH COMPOSITIONS INCORPORATING A PARTICULATE FILLER COMPONENT

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates to compositions and methods for manufacturing thermoplastic starch compositions and articles made therefrom. More particularly, the present invention relates to thermoplastic starch compositions that include a particulate filler component. The thermoplastic starch compositions may optionally include one or more additional thermoplastic polymers blended therewith and fibers for reinforcement.

2. The Relevant Technology

A. Sheets, Containers, and Other Articles Made From Paper, Plastic, Glass and Metal.

Materials such as paper, paperboard, plastic, polystyrene, and metals are presently used in enormous quantity as printed materials, labels, mats, and in the manufacture of other articles such as containers, separators, dividers, envelopes, lids, tops, cans, and other packaging materials. Advanced processing and packaging techniques presently allow an enormous variety of liquid and solid goods to be stored, packaged, or shipped while being protected from harmful elements.

Containers and other packaging materials protect goods from environmental influences and distribution damage, particularly from chemical and physical influences. Packaging helps protect an enormous variety of goods from gases, moisture, light, microorganisms, vermin, physical shock, crushing forces, vibration, leaking, or spilling. Some packaging materials also provide a medium for the dissemination of information to the consumer, such as the origin of manufacture, contents, advertising, instructions, brand identification, and pricing.

Typically, most containers and cups (including disposable containers) are made from paper, paperboard, plastic, polystyrene, glass and metal materials. Each year over 100 billion aluminum cans, billions of glass bottles and thousands of tons of paper and plastic are used in storing and dispensing soft drinks, juices, processed foods, grains, beer, etc. Outside of the food and beverage industry, packaging containers (and especially disposable containers made from such materials are ubiquitous. Paper for printing, writing, and photocopying, as well as magazines, newspapers, books, wrappers, and other flat items made primarily from tree derived paper sheets are also manufactured each year in enormous quantities. In the United States alone, approximately 5½ million tons of paper are consumed each year for packaging purposes, which represents only about 15% of the total annual domestic paper production.

Recently there has been a debate as to which of these materials (e.g., paper, paperboard, plastic, polystyrene, or metal) is most damaging to the environment. Consciousness-raising organizations have convinced many people to substitute one material for another in order to be more environmentally "correct." The debate often misses the point that each of these materials has its own unique environmental weaknesses. One material may appear superior to another when viewed in light of a particular environmental problem, while ignoring different, often larger, problems associated with the supposedly preferred material (e.g., whereas paper is more biodegradable than plastics and polystyrene, paper is far more polluting to the environment to manufacture).

The debate should not be directed to which of these materials is more or less harmful to the environment, but rather toward asking whether an alternative material can be developed which will solve most, if not all, of the various environmental problems associated with each of these presently used materials.

B. Starch.

Starch is a plentiful, inexpensive and renewable material that is found in a large variety of plant sources, such as grains, tubers, fruits, and the like. In many cases, starch is discarded as an unwanted byproduct of food processing. However, because starch is readily biodegradable it does not persist in the environment as a harmful material when disposed of. Perhaps the only harm that starch might cause is that it can put unwanted nutrients into the water or soil into which it is discarded, which could attract and facilitate the proliferation of certain unwanted organisms. It is this quality as a nutrient, though, that greatly facilitates the breakdown and elimination of starch from the environment.

Because of the biodegradable nature of starch many have attempted to incorporate starch into a variety of materials in order to improve the environmental desirability of such materials. Starch has been incorporated into multi-component compositions in various forms, including as a filler, binder, or as a constituent within thermoplastic polymer blends. In addition, some have attempted to utilize starch alone as a thermoplastic material, although with limited success due to the tendency of starch to form retrograde crystallization products upon resolidifying, which crystallization products often lack appropriate mechanical properties.

Starch may be added as an inert filler, typically in its native, unmodified state, which is a generally water-insoluble, granular material. In such cases, the starch granules will normally behave as any other solid particulate filler and will contribute little, if any, in terms of improving the mechanical properties of the resulting material. Alternatively, starch that has been gelatinized, dried, and then ground into a powder may also be added as a particulate filler. Although starch may be added as a filler, its more interesting and technologically challenging uses have been in the area of using starch as a binder, as a thermoplastically processible constituent within thermoplastic polymer blends, and as a thermoplastic material by itself.

Although the alternative uses of starch as a water-soluble binder or as a thermoplastic material generally require significantly different compositional formulations and process conditions in order to successfully process them as intended, they have the common requirement that the native starch granules must in some way be transformed or altered from being in a granular or particulate state to being in a molten or plastic state, such as by dissolution or gelation within a solvent or by being heated to form a starch melt. Because native starch has a melting point that approaches the decomposition temperature, it is virtually impossible to form a starch melt without the addition of plasticizers, solvents or other components that allow the starch to become molten, solvated or otherwise liquified into a plastic state at a temperature that is safely below the decomposition temperature.

Starch can be used as a "binder" in order to glue or otherwise adhere other solid constituents together to form a heterogenous mixture of different components. At some point before or during the molding phase, the starch is typically dissolved or gelatinized in an appropriate solvent, such as water, in order for it to become a liquid or gel. This

allows the initially granular starch to become a flowable or plastic material into which the other components can be dispersed. Upon resolidification of the gelatinized starch, typically by removing enough of the water by evaporation so that the starch recrystallizes or otherwise dries out, the starch forms a solid or semi-solid binding matrix that can bind the remaining components together. Examples of patents that teach the use of starch as a binder and, in particular, processes for molding articles from aqueous starch mixtures include U.S. Pat. No. 5,660,900 to Andersen et al.; U.S. Pat. No. 5,683,772 to Andersen et al.; U.S. Pat. No. 5,709,827 to Andersen et al.; U.S. Pat. No. 5,868,824; and U.S. Pat. No. 5,376,320 to Tiefenbacher et al. For purposes of disclosing compositions, methods, and systems for molding aqueous starch mixtures that are subsequently dried so as to form a binding matrix of dried starch which binds together discrete solid materials such as fibers and/or particulate fillers, the foregoing patents are incorporated herein by specific reference.

Related to the process of molding aqueous starch mixtures is the formation of sheets having properties similar to conventional paper and paperboard by methods that do not require the use and subsequent removal of the huge quantities of water required in conventional paper-making processes. Examples of compositions, processes, and systems; for continuously manufacturing sheets from aqueous starch-based mixtures in a manner that does not utilize conventional drainage or dewatering are set forth in U.S. Pat. No. 5,736,209 to Andersen et al. and U.S. Pat. No. 5,810,961. For purposes of disclosing composition, methods and systems for the formation of sheets from aqueous starch-based mixtures, the foregoing patents are incorporated herein by specific reference.

Many have also attempted to use starch as a thermoplastic material, either alone or as a component within thermoplastic blends. Native starch does not typically behave as a thermoplastic material by itself but must be heated in the presence of some kind of plasticizer. Typically, the plasticizer must be a liquid (at least when raised to the resulting chemically compatible with starch, which is itself highly polar due to the existence of hydroxyl groups on approximately half of the carbon atoms. Typically, plasticizers used to assist the formation of starch melts have been either highly volatile liquids at the melting point, such as water, or low volatile liquids, such as glycerin.

Starch melts using water as the plasticizing solvent have been referred in the art as "destructured starch". Starch is said to be "destructured" because it ceases to be a solid granular particulate as found in its native state. Moreover, it is said to be "destructured" because the dissolution or melting of starch in the presence of water is an irreversible process. Starch that has been dissolved into or melted in the presence of water can never return to its native, granular state. Upon resolidification of a melt of destructurized starch, typically by cooling below its melting or softening point, it will yield an essentially amorphous or semicrystalline starch material that is self-supporting or "form stable", but only so long as the water content is kept above at least 5% by weight of the starch and water mixture during the entire process including during cooling, preferably above at least 10%. Otherwise, the starch will tend to recrystallize into a brittle material instead of forming a more amorphous and less brittle solid.

The use of "destructured starch" as a commercial thermoplastic material has been limited for a number of reasons, including difficulty in processing, poor long term mechanical properties, high sensitivity to fluctuations in ambient

moisture, including poor dimensional stability, and the difficulty of forming homogeneous blends of destructurized starch with more hydrophobic polymers that are less sensitive to fluctuations in moisture. Examples of patents that disclose the manufacture of "destructured starch" and blends of destructurized starch and other polymers include U.S. Pat. No. 4,673,438 to Wittwer et al.; U.S. Pat. No. 4,900,361 to Sachetto et al.; U.S. Pat. No. 5,095,054 to Lay et al.; U.S. Pat. No. 5,256,711 to Tokiwa et al.; U.S. Pat. No. 5,275,774 to Bahr et al.; U.S. Pat. No. 5,382,611 to Stepto et al.; U.S. Pat. No. 5,405,564 to Stepto et al.; and U.S. Pat. No. 5,427,614 to Wittwer et al. For purposes of disclosing compositions and methods for manufacturing "destructured starch" compositions, including blends of "destructured starch" and other polymers, the foregoing patents are incorporated herein by specific reference.

Others have taught that it is preferable to greatly reduce the amount of water in starch melts by replacing the water inherently found in starch with an appropriate low volatile plasticizer capable of causing starch to form a thermoplastic melt below its decomposition temperature, such as glycerin, polyalkylene oxides, mono- and diacetates of glycerin, sorbitol, other sugar alcohols, and citrates. This allows for improved processability, greater mechanical strength, better dimensional stability over time, and greater ease in blending the starch melt with other polymers compared to "destructured starch". Thermoplastic starch materials in which most or all of the water has been replaced by a low volatile plasticizer, either before or during processing, have been variously referred to as "thermoplastically processible starch" and "thermoplastic starch".

Water can be removed before processing by using starch that has been predried so as to remove at least a portion of the natural water content. Alternatively, water can be removed during processing by degassing or venting the molten mixture, such as by means of an extruder equipped with venting or degassing means. Examples of patents that teach the manufacture of thermoplastically processible starch, including blends of thermoplastic starch and other polymers, include U.S. Pat. No. 5,362,777 to Tomka; U.S. Pat. No. 5,314,934 to Tomka; U.S. Pat. No. 5,280,055 to Tomka; U.S. Pat. No. 5,415,827 to Tomka; U.S. Pat. No. 5,525,281 to Lörcks et al.; U.S. Pat. No. 5,663,216 to Tomka; U.S. Pat. No. 5,705,536 to Tomka; U.S. Pat. No. 5,770,137 to Lörcks et al.; and U.S. Pat. No. 5,844,023 to Tomka. For purposes of disclosing compositions and methods for the manufacture of thermoplastic starch compositions, blends thereof, and articles of manufacture therefrom, the foregoing patents are incorporated herein by specific reference.

Still others have manufactured thermoplastic starch blends in which native starch is initially blended with a small quantity of water together and a less volatile plasticizer such as glycerin in order to form starch melts that are subjected to a degassing procedure prior to cooling and solidification in order to remove substantially all of the water therefrom. Examples of such patents include U.S. Pat. No. 5,412,005 to Bastioli et al.; U.S. Pat. No. 5,280,055 to Bastioli et al.; U.S. Pat. No. 5,288,765 to Bastioli et al.; U.S. Pat. No. 5,262,458 to Bastioli et al.; 5,462,980 to Bastioli et al.; and U.S. Pat. No. 5,512,378 to Bastioli et al.

Regardless of whether water or another plasticizer is used to form a starch melt, all destructurized and thermoplastic starch materials have been limited in the market place by the inherent mechanical limitations of starch melts and their relatively high cost. Although many have attempted for years to discover the "perfect" starch/polymer blend that would yield an environmentally sound polymer while, at the

same time, fulfilling desired mechanical and cost criteria, such a combination has not yet been achieved. The reason for this is that the emphasis has been on finding the optimal synthetic polymer or mixture of synthetic polymers and other admixtures in order to thereby "optimize" the properties of the starch/polymer blend. One drawback is that most of the synthetic polymers and other admixtures are themselves significantly more expensive than starch, which tends to increase the cost of such polymer blends compared to starch melts. Another drawback is that such additives will only be able to marginally alter the mechanical properties of the starch/polymer blends when viewed from a materials science perspective.

In spite of the inherent economic limitations associated with thermoplastic starch blends, the focus of researchers has remained rigidly fixed on the goal of finding the "perfect" thermoplastic polymer or other admixture that will yield the "perfect" starch-polymer blend. Although extremely inexpensive fillers such as naturally occurring mineral materials have been added to concrete and other building materials, their use as an inexpensive filler within destructurized or thermoplastic starch systems has been largely ignored. Although the aforementioned U.S. Pat. No. 5,362,777 to Tomka discloses the inclusion of an inorganic filler, such filler component is limited to concentrations of 3% or less by weight. Likewise, the aforementioned U.S. Pat. No. 5,427,614 to Wittwer et al. discloses the use of an inorganic "texturizing agent" having a concentration of 1% or less. At such low concentrations, inorganic fillers will only have a marginal impact on the cost and mechanical characteristics of the thermoplastic or destructurized starch materials disclosed therein.

Based on the foregoing, what are needed are improved thermoplastic starch compositions and methods for manufacturing low cost, environmentally friendly sheets, films, and molded articles having appropriate mechanical properties similar to, e.g., paper, paperboard, polystyrene, other plastics, metal sheets, and the like.

It would be a significant improvement in the art if such thermoplastic starch compositions allowed for the formation of a variety of containers or other articles using existing manufacturing equipment and techniques presently used to form articles from paper, polymer films, or moldable plastic materials.

It would yet be an advancement in the art if such environmentally friendly thermoplastic starch compositions could be formed from compositions that only included a fraction of the starch content compared to other starch-based compositions presently being utilized.

It would be a significant improvement in the art if such thermoplastic starch compositions yielded articles that were readily biodegradable and/or degradable into substances commonly found in the earth.

From a practical point of view, it would be a significant improvement to provide thermoplastic starch compositions and methods which allowed for the manufacture of sheets, containers, and other articles at a cost that was comparable to or even lower than the cost of existing methods of manufacturing articles from paper, plastics, or other materials.

It would be a further advancement in the art to provide thermoplastic starch compositions and methods which allowed for the inclusion of less organic polymer materials while overcoming many of the problems associated with compositions based on starch melts.

It would also be a tremendous advancement in the art to provide thermoplastic starch compositions and methods

which allowed for the inclusion of significant quantities of an inorganic filler and, optionally fibrous materials, both organic and inorganic, within such starch compositions.

In addition, it would be an advancement in the art to provide thermoplastic starch compositions that had improved physical properties, such as increased thermal stability, increased modulus of elasticity, compressive strength, and toughness compared to conventional thermoplastic starch compositions.

Such thermoplastic starch compositions and methods for manufacturing starch-based sheets, films articles therefrom, and molded articles are disclosed and claimed herein.

SUMMARY AND OBJECTS OF THE INVENTION

The present invention is directed to compositions and methods for manufacturing thermoplastic starch compositions having a particulate filler and, optionally, fiber-reinforcement. Such "thermoplastic starch compositions" having a particulate filler can be shaped into a wide variety of articles of manufacture in a manner similar to conventional thermoplastic materials.

The raw material that is used to make the thermoplastic starch compositions of the present invention preferably comprises native, ungelatinized starch granules, although one or more starch derivatives may also be used, either alone or in combination with native starch. Native starch granules are made thermoplastic by mixing and heating in the presence of an appropriate plasticizer to form a starch melt. The starch melt is then blended with on, or more non-starch materials in order to improve the properties and/or reduce the cost of the resulting thermoplastic starch composition. At a minimum, a particulate filler component is blended with the starch melt, preferably an inexpensive, naturally occurring mineral particulate filler ("inorganic filler"). In order to increase the tensile strength and other desirable mechanical properties of the starch/filler blend, other admixtures such as fibers, one or more synthetic polymers, cross-linking agents, softening agents, and the like may be included within the thermoplastic starch compositions.

In order to create the necessary conditions required to form a starch melt, the initially solid starch granules are mixed at high shear together with an appropriate admixture, such as a lower volatile plasticizer or a more volatile plasticizing solvent, at a temperature and pressure sufficient to form the starch melt. In one embodiment, the starch and admixture are blended within the barrel of a screw or auger extruder. The extruder is heated and the screw auger within the extruder barrel is rotated in order to heat and blend the starch and plasticizer together under relatively high shear conditions to thereby cause the starch to form a melt. Because the melting point of native starch normally approaches decomposition temperature, it is necessary to melt native starch in the presence of a plasticizing admixture in order to form a workable and plastic starch melt at a temperature below the decomposition temperature. In the case where a low volatile plasticizer is used, i.e., one that has a vapor pressure of less than about 1 bar when heated to the melt temperature of the starch, it may be possible to use any appropriate high shear mixing apparatus, such as a high speed food mixer. However, in the case where a more volatile plasticizing solvent such as water is used, and where the melting point of the starch will cause the more volatile plasticizing solvent to rapidly vaporize, it may be necessary to maintain enough internal pressure, such as within an extruder barrel, to keep the plasticizer from violently

expanding and impeding the process of forming the starch melt. Some or all of the volatile plasticizing solvent may be removed by venting.

Before, during or after the formation of the starch melt, appropriate additives may be blended with the starch melt. The resulting thermoplastic starch composition is either extruded or otherwise formed into appropriately sized beads, granules, or other storable and feedable materials, or else it is immediately shaped into the desired article, such as sheets, films, or molded articles. In many cases, methods and apparatus commonly used in the plastics industry may be employed with only modest, or even no, modification in some cases.

The molten thermoplastic starch compositions are caused to solidify by cooling to below their softening or melting point. The terms "softening point" or "melting point" shall refer to the temperature or temperature range above which a particular thermoplastic starch composition is sufficiently plastic and flowable such that it can be molded or formed into a desired shape, and below which the composition solidifies to the point of being approximately form stable or self-supporting. The quantity of plasticizer or other admixtures can be adjusted to yield thermoplastic starch compositions having a softening or melting point greater than about 40° C. Preferably, the softening or melting point will be in a range from about 60° C. to about 240° C., more preferably in a range from about 80° C. to about 220° C., and most preferably in a range from about 100° C. to about 200° C.

Adding an inorganic filler material to the starch melt greatly decreases the cost and, in some cases, even improves the desired mechanical properties, of the thermoplastic starch compositions of the present invention. In order to increase the concentration of inorganic filler within a thermoplastic starch composition it will generally be desirable to increase the ratio of the volume of the inorganic filler compared to its surface area. Thus, it will generally be preferable to select inorganic filler particles in a manner that reduces their specific surface area. One way to do this is to select particles that have more uniform and less irregular surfaces. For example, spherical particles have a much lower surface area to volume ratio (i.e., lower specific surface area) than highly irregularly shaped particles. Another strategy for decreasing the specific surface area of particle system is to use larger particles that have a lower surface to volume ratio. Larger particles can also be blended with smaller particles to thereby allow the smaller particles to occupy the spaces between the larger particles, which increases the particle packing density of the particulate filler phase.

By selecting an inorganic filler that tends to minimize, or at least optimize, the specific surface area of the filler particles, it is possible to increase the quantity of inorganic filler that can be added to the thermoplastic starch compositions, while maintaining appropriate rheological characteristics of the starch melt during molding and also maximizing the strength of the final solidified thermoplastic starch composition. The reason for this is that particles having lower specific surface area have a lower overall surface that must come into contact with the thermoplastic starch melt, which allows for more efficient use of the binder. Moreover, the use of particle packing techniques further allows for more efficient use of the thermoplastic starch melt since the spaces that would otherwise be occupied entirely by the starch melt will instead be occupied in large measure by the smaller filler particles. Increasing the particle packing density generally increases the amount of inorganic filler that may be added while reducing the negative impact on the rheological and mechanical properties of the composition.

In view of the foregoing, it is now possible to manufacture highly inorganically filled thermoplastic starch compositions having improved mechanical properties. Of equal or greater importance is the fact that space or volume once occupied by the relatively expensive thermoplastic starch binder can now be occupied by the generally far less expensive inorganic filler component to thereby yield a final thermoplastic starch composition having a greatly reduced volume-to-cost (or mass-to-cost) ratio.

In general, the inorganic filler may be included within the thermoplastic starch compositions of the present invention in a broad range from about 5% by volume up to about 90% by volume of the thermoplastic starch composition. Depending on the specific gravity of the inorganic filler, the filler may be included in an amount in a range from about 5% to about 95% by weight of the thermoplastic starch compositions of the invention. In order for the filler to significantly reduce the cost of the thermoplastic starch composition, the inorganic filler will preferably be included in an amount greater than about 15% by weight of the thermoplastic starch composition, more preferably in an amount greater than about 25% by weight, more especially preferably in an amount greater than about 35% by weight, and most preferably in an amount greater than about 50% by weight.

In some cases, it may be desirable to include a fibrous material as a reinforcing component in order to improve the strength properties of the final thermoplastic starch compositions. In general, fibers tend to increase the tensile strength, toughness, and fracture energy of the resulting thermoplastic starch compositions. Although fibers are generally difficult to disperse within liquids unless the liquid is included in an overwhelmingly high proportion compared to the fibers, fibers may in fact be blended within the thermoplastic starch compositions of the present invention due to the shearing action to which the starch will typically be exposed during the melt process. In addition, because starch melts typically have a fairly high viscosity, they are able to efficiently transfer the shearing forces from the mixing apparatus down to the fiber level in order to separate the fibers and keep them from agglomerating together, as might occur by mixing fibers using a nonviscous, Newtonian fluid such as water.

In order to maximize the strength properties that may be imparted by the fibrous material, it will generally be preferable to include fibers having a relatively high aspect ratio, typically greater than about 10:1, preferably greater than about 25:1, more preferably greater than about 100:1 and most preferably greater than about 250:1. Examples of useful fiber; include those derived from wood, plant sources, mineral fibers, and polymer fibers.

Nevertheless, it may be desirable to add particulate fibrous fillers that may behave in a similar fashion to inorganic mineral fillers. Such particulate fibrous materials include, for example, sawdust, wood flour, waste bran materials from grain processing, and other generally inexpensive and plentiful fibrous particulates. One advantage of fibrous particulates is the fact that they comprise cellulose, which is chemically similar to starch and which would therefore be generally very compatible with the starch binder. Within the scope of fibrous materials that could be included would be flakes or flake-like materials, such as metallic flakes.

The fibrous material may include filaments, fabrics, mesh or mats that are coextruded, or otherwise impregnated, with the thermoplastic starch compositions of the present invention.

In order to improve the strength and other mechanical properties of the thermoplastic starch compositions of the

present invention, the fibrous material may be included in a broad range from 0% to about 90% by weight of the thermoplastic starch-based composition. Preferably, the fibrous material will be included in an amount in a range from about 3% to about 80% by weight, more preferably in a range from about 5% to about 60%, and most preferably in a range from about 10% to about 30% by weight of the thermoplastic starch compositions.

It may also be preferable in many cases to blend one or more other thermoplastic polymers with the starch melts in order to form a starch/polymer blend. Such other thermoplastic polymers may be added in order to improve the mechanical properties of the thermoplastic starch compositions, reduce the sensitivity of such materials to fluctuations in ambient moisture, make such materials more water impermeable, increase the strength and improve other mechanical properties of the resulting thermoplastic starch compositions, and/or assist in preventing the formation of retrograde starch crystallization products upon solidification.

The thermoplastic starch materials of the present invention may include a wide variety of different components that can impart greatly varying mechanical and other properties to the final thermoplastic starch compositions. Therefore, based on the teachings of the disclosure, one of ordinary skill in the art will be able to design a thermoplastic starch composition having any one of a wide variety of mechanical, chemical, or other properties in order to satisfy the design criteria of the final articles to be manufactured from the thermoplastic starch compositions. More particularly, based on the present disclosure, one of ordinary skill in the art will be able to select from among the various components in order to maximize the desired mechanical properties while minimizing the cost of the thermoplastic starch compositions of the present invention.

Virtually any thermoplastic material may be blended with a starch melt in order to form the thermoplastic starch compositions of the present invention. Nevertheless, preferred polymers include synthetic or naturally derived polymers that are sufficiently compatible with starch in order to form a substantially homogeneously blended starch/polymer mixture. Increasing the homogeneous nature of the starch/polymer blends will tend to create a material having more uniformly and predictably distributed mechanical properties throughout the material. More preferred synthetic polymers include those that are able to react with and form mechanical bonds with at least a portion of the starch molecules within the melt. Obviously, reacting the synthetic polymer with the starch will, by definition, form a more homogeneous final thermoplastic starch composition.

Due to the fact that the reaction sites located along the starch molecular chain are hydroxyl groups, the most likely reaction between starch and a synthetic polymer will involve some kind of reaction between the hydroxyl groups and the synthetic polymer, including but not limited to esterification, etherification, substitution, the formation of acetals or ketals, and the like. Because the existence of substantial quantities of water will tend to inhibit condensation reactions or cross-condensation reactions (e.g., cross esterification) by driving the equilibrium toward hydrolysis, it will be preferable when utilizing synthetic polymers to be condensed or cross-condensed with the starch to eliminate excess water that could inhibit the condensation reactions. One way to do this is to use pre-dried starch, such as starch that has been dried by heating in order to drive off a significant portion of the water that naturally occurs in starch. Starch typically contains about 10–20% moisture by weight, which is pref-

erably reduced to below about 10%, more preferably to below about 5% and most preferably to below about 3% by weight prior to forming the starch melt. Alternatively, the excess water can be removed from the starch melt by evaporation prior to or while blending the starch melt with the synthetic polymer. Finally, it may be preferable to vent, chemically or physically scavenge, or otherwise provide for the removal of water molecules that are released during heating to form the starch melt and/or that may be formed during condensation reactions in order to drive the equilibrium of the condensation reaction in the forward direction.

Once the thermoplastic starch compositions have been made, they can be stored as beads, granulates or other appropriate shapes. The thermoplastic starch beads, granulates, and the like, or a freshly prepared batch of a thermoplastic starch composition according to the invention, can be molded using any conventional molding means known in the art for shaping thermoplastics and other materials, including but not limited to die press molding, injection molding, blow molding, vacuum forming, rolling, extrusion, film blowing, laminating, coating, and the like.

Blowing or expansion agents may be included within the thermoplastic starch compositions so as to yield final molded articles that are foamed, or which otherwise include a substantial quantity of void spaces. For example, water may be used to yield a foamed composition in view of the operating temperatures. Fibers premoistened with water can provide the water for such expansion or foaming.

In light of the foregoing, it is an object of the present invention to provide improved thermoplastic starch compositions and methods for manufacturing low cost, environmentally friendly sheets, films, articles made therefrom, and molded articles having appropriate mechanical properties similar to, e.g., paper, paperboard, polystyrene, plastic, metal sheets, and the like.

It is another object of the present invention that such thermoplastic starch compositions allow for the formation of a variety of containers and other articles using existing manufacturing equipment and techniques presently used to form articles from paper, polymer films, or moldable plastic materials.

It is a further object of the present invention that such environmentally friendly thermoplastic starch compositions can be formed from compositions that only include a fraction of the starch content compared to other starch-based compositions presently being utilized.

It is yet an additional object that such compositions yield articles that are readily biodegradable and/or degradable into substances commonly found on the earth.

It is a further object and feature to provide thermoplastic starch compositions and methods which allow for the manufacture of sheets, containers and other articles at a cost that is comparable to, or even lower than, the cost of existing methods of manufacturing articles from paper, plastics, or other materials.

It is yet another object to provide thermoplastic starch compositions and methods which allow for the inclusion of less organic polymer materials while overcoming many of the problems associated with conventional starch melts.

It is a further object to provide thermoplastic starch compositions and methods which allow for the inclusion of significant quantities of an inorganic filler and, optionally fibrous materials, either organic or inorganic, within such thermoplastic starch compositions.

It is an additional object and feature of the invention to provide thermoplastic starch compositions that have

improved physical properties, such as increased thermal stability, increased modulus of elasticity, compressive strength, and toughness compared to conventional thermoplastic starch compositions.

These and other objects and features of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

I. Introduction and General Definitions

The present invention encompasses thermoplastic starch compositions that, at a minimum, include starch, a plasticizer, and an inorganic mineral filler. Such compositions may also include fibers, synthetic polymers, and other admixtures in order to impart desired properties to the composition while in a melt stage as well as the final resolidified composition and articles manufactured therefrom. The inorganically filled, thermoplastic starch compositions can be shaped into a wide variety of articles of manufacture much like conventional thermoplastic materials.

The thermoplastic starch compositions of the present invention can generally be described as comprising multi-component, multi-scale, micro-composites. By carefully incorporating a variety of different materials capable of imparting discrete, yet synergistically related, properties, it is possible to create a unique class or range of micro-composites having remarkable properties of strength, toughness, environmental soundness, mass-productibility, and low cost.

The term "multi-component" refers to the fact that the thermoplastic starch compositions typically include two or more chemically or physically distinct materials or phases, such as the binding matrix comprising, at a minimum, a starch melt formed by plasticizing starch with a plasticizer, a particulate filler and optional admixtures, such as fibers for reinforcement auxiliary polymers for added strength and water-resistance and void spaces for lightweight and/or insulation properties. Each of these broad categories of materials imparts one or more unique properties to the final thermoplastic starch compositions made therefrom, as well as to the sheets, films and other articles manufactured therefrom. Within these broad categories it is possible to further include different components such as, for example, two or more types of inorganic fillers, fibers, and synthetic organic polymers, which can impart different yet complementary properties to the inventive thermoplastic starch compositions. This allows for the specific engineering of desired properties within the final articles in conjunction with the manufacturing process.

The multi-component (and hence, multi-property) nature of the thermoplastic starch compositions of the present invention is a significant departure from conventional materials, such as plastic, polystyrene, paper, or metal, which are essentially single component systems. Sheets, films, or molded articles made from single component materials are generally limited to having the particular properties of the material from which they are made. For example, films or sheets that are brittle generally cannot be bent or folded without damaging the films or sheets, while films or sheets that are flexible are insufficiently rigid to provide other desired mechanical properties. In contrast, the multi-component nature of the materials of the present

invention allows for the introduction of multiple and/or specially engineered properties to allow for the manufacture of an almost endless variety of articles from such thermoplastic starch compositions.

The term "multi-scale" refers to fact that the compositions and materials of the present invention are definable at different levels or scales. Specifically, within the thermoplastic starch compositions of the present invention there is typically a macro-component composition in the range from about 10 nanometers to as high as about 10 mm, a micro-component composition in the range of about 1 micron to about 100 microns, and a submicron component. Although these levels may not be fractal, they are usually very similar to each other, and homogeneous and uniform within each level.

In some cases, the materials may be reinforced with fibers. The term "fiber-reinforced" is self-explanatory, although the key term is "reinforced", which clearly distinguishes the compositions of the present invention from conventional paper or paper products. Conventional paper relies on "web" physics, or intertwining of fibers, to provide the structural matrix and mass, as well as the binding, of the paper. However, the binding matrix in the compositions of the present invention involves the interaction between The thermoplastic starch phase, inorganic mineral filler component, optional fibers, and other optional components. The fibers act primarily as a reinforcing component to specifically add tensile strength, toughness, and flexibility but are not joined together by web physics to any substantial degree.

Finally, the term "micro-composite" refers to the fact that the thermoplastic starch compositions are not merely a compound or mixture but a designed matrix of specific, discrete materials on a micro-level, which are of different sizes, shapes, and chemical make-up. The materials are sufficiently well bound and interactive so that the unique properties of each are fully evidenced in the final composite (e.g., the tensile strength of the composition has a direct correlation to the tensile strength of the fibers and thermoplastic starch phase).

In light of these definitions and principles, thermoplastic starch materials can be combined with inorganic fillers and other components and molded into a variety of products, including films, sheets, and molded articles having properties similar to those of conventional thermoplastic or paper materials. Articles made therefrom can substitute for articles made from paper, plastic, polystyrene, and even metal. Films and sheets can be cut and formed (such as by bending, folding or rolling) into a variety of containers and other articles of manufacture. The thermoplastic starch compositions of the invention, including sheets, films, or articles molded therefrom, are particularly useful in the mass production of disposable containers and other packaging material, such as used in the fast food industry.

A. Thermoplastic Materials

The term "thermoplastic materials" is understood in the art and used herein to denote compositions and materials that are generally capable of repeatedly softening when appropriately heated and hardening when subsequently cooled. "Thermoplastic materials" are generally in a solid or form stable state below the melting point or softening range, while generally being in a plastic or flowable state above the melting point or softening range. The term "solid" means that the material is sufficiently hardened, nonplastic or nonflowable such that it will substantially maintain its shape without external support. Of course, "solid" materials may have a degree of resilience, bendability or deformability and

yet maintain their characteristic as being a "solid". As used in the specification and appended claims, the term "melting point" shall be understood to refer to both the discrete melting points of more crystalline polymers and the melting or softening ranges of more amorphous polymers, unless otherwise specified.

The terms "plastic" and "flowable" are used in conjunction with materials that can be molded or otherwise shaped or deformed without causing significant damage to the structural matrix of the material upon resolidification. Thus, while a solid material may be bent or otherwise deformed, there is a point after which further movement or deformation could cause the structural matrix to rupture, crack, or otherwise weaken irreversibly. Plastic or flowable materials, on the other hand, are characterized as being able to be shaped and deformed as desired while yielding a final solidified article having the same general strength properties upon solidification regardless of the degree of deformation while in a plastic state when normalized for variables such as thickness, size, shape, texture, molecular orientations, and the like. One of ordinary skill in the art will generally know by observation and experience whether a given thermoplastic material should be considered to be a "solid" or "nonplastic" on the one hand or "plastic" or "flowable".

A thermoplastic material is characterized in that it may be shaped into a desired article by first heating the material to a temperature above its melting point or softening range to form a flowable or plastic melt. The thermoplastic melt may then be shaped into a desired article. Thereafter, or substantially at the same time of shaping, the shaped material is cooled sufficiently to cause it to harden or solidify and thereby form the desired article or intermediate material. The intermediate material may be further shaped or manipulated by reheating it to form a melt phase and then cooling to resolidify the shaped material.

The degree of crystallinity can affect whether or not a thermoplastic polymer has a distinct or abrupt melting point. In general, the more crystalline a polymer is, the more distinct will be its melting point. Conversely, more amorphous polymers tend to soften, melt and solidify over a range of temperatures. Thus, amorphous polymers do not have a distinct melting point but rather a softening or melting range. Because of this, more amorphous polymers have greater "melt stability". That is, they can be melted and then shaped under conditions of high shear and pressure over a relatively broad range of temperatures without abruptly solidifying like more crystalline polymers. The softening or melting range generally becomes even broader as variability in the molecular weight of the individual polymer chains increases, which tends to further inhibit crystallization of the polymer molecules.

The temperature at which a more amorphous polymer becomes soft enough to be shaped is generally significantly lower than the melting point of a more crystalline form of the same polymer. In other words, the softening or melting range of a more amorphous polymer may be substantially lower than the melting point of a more crystalline form of the same polymer. Thus, more amorphous polymers can often be shaped at lower temperatures compared to similar polymers that are more crystalline. Conversely, more crystalline polymers may solidify more abruptly when cooled to below the melting point but will also exhibit greater dimensional stability when subsequently subjected to heat. More amorphous polymers tend to have greater flexibility and bending endurance while more crystalline polymers are more rigid and have a greater Young's modulus.

Because more crystalline polymers have a more abrupt melting point above which the polymer is plastic and

flowable and below which the polymer is a crystalline solid, further cooling of a crystalline polymer below its melting point will typically cause only minor incremental changes in its physical properties, if at all. On the other hand, more amorphous polymers, in addition to having a softening range, have what is known in the art as a "glass transition temperature" somewhere below the softening point or melt temperature at which they first become solid and dimensionally stable. Below the glass transition, temperature, amorphous polymers become considerably more rigid and brittle, while above this temperature they tend to be increasingly flexible and elastic. Thus, amorphous polymer exhibit greater dimensional stability and have increased modulus of elasticity below the glass, transition temperature. Conversely, they are more flexible, pliable and elastic above the glass transition temperature, although they may still have sufficient dimensional stability and resilience so as to be considered to be a "solid". Although the glass transition temperature is often reported as a single value, it is known that the glass transition may actually occur over a temperature range and it is attributed a kinetic meaning.

In some cases it may be possible to control the degree of crystallinity of a polymer by the manner in which a polymer melt is cooled. Cooling the polymer melt gradually as the temperature approaches the melting or softening point will increase the tendency of the polymer to become more crystalline. This is because slowly cooling the polymer allows the individual molecules to reorder themselves into more of a crystalline structure before the polymer actually becomes solid. Conversely, cooling a polymer melt more rapidly tends to maintain the polymer in a less crystalline and more amorphous state by quickly "freezing" (sometimes referred to as "quenching") the individual molecules in a more random state before they have an opportunity to arrange themselves into a more crystalline structure.

In general, the term "thermoplastic material" is distinguished from "thermoset materials", which generally cannot generally be resoftened by reheating once they have been set into a permanent shape by heating or by the action of heat and pressure. Nevertheless, in the context of the present invention, it should be understood that the term "thermoplastic materials" may include a fraction of some materials which, by themselves, are not necessarily completely remeltable once solidified following initial melting, although in most cases the overall thermoplastic starch materials will exhibit classic thermoplastic behavior.

The term "thermoplastic starch composition", as used in the specification and the appended claims, is broadly defined to include any thermoplastic composition or blend having thermoplastic starch as a constituent. The only other limitation of the term "thermoplastic starch composition" within the context of the present invention is that the composition will include a filler component as a discrete phase that is dispersed throughout the thermoplastic phase. Hence, the term "thermoplastic starch composition" is limited to those thermoplastic starch materials that include the aforementioned filler. The filler component may include an organic filler, an inorganic filler, or both. In its broadest sense, the term "filler" may include both fibrous materials and particulate particles. The thermoplastic starch compositions may also optionally include other polymer materials for altering the properties of the thermoplastic phase, cross-linking agents, phase mediators, softeners, humectants, and other admixtures for engineering desired properties into the final thermoplastic starch composition.

Because native starch is generally incapable of behaving as a thermoplastic material by itself, or by itself in combi-

nation with a particulate filler, it will generally be understood that the starch melt component will further include some kind of melt-initiating agent that can cause the starch to behave in a thermoplastic manner. In order to distinguish the thermoplastic starch component from the overall thermoplastic starch composition, the terms "thermoplastic starch" or "thermoplastic starch component" shall refer to the fraction of the overall thermoplastic starch composition comprising a starch melt. The term "starch melt" shall be broadly understood to include starches that are in a molten state, as well as starch materials that have previously undergone a melt but that have subsequently become solidified. Thus, the term "starch melt" shall be synonymous with any thermoplastically processible starch material, whether in a molten or solid state, that was originally formed by melting starch in the presence of a plasticizer.

Both low volatile plasticizers having a vapor pressure of less than 1 bar at the melt temperature of the thermoplastic starch composition (e.g., glycerin and sorbitol) and volatile solvents having a vapor pressure greater than 1 bar at the melt temperature (e.g., water) fall within the general classification of "plasticizers" and "melt initiation agents".

The thermoplastic starch compositions comprise a heterogeneous, though a preferably homogeneously mixed, mixture of at least two discrete phases, namely a thermoplastic phase, a solid filler phase, and other optional phases. The thermoplastic phase will typically comprise starch, a plasticizer, and optionally one or more other polymer materials or liquids that can be mixed or interspersed sufficiently with the starch so as to essentially constitute a single "thermoplastic phase". The thermoplastic phase, whether a homogeneous material or a heterogeneous blend of hydrophobic and hydrophilic thermoplastic phases, is characterized as generally being capable of forming a melt by heating to above a temperature, a temperature range, or a series of temperatures or temperature ranges and then resolidifying when cooled sufficiently. As such, the thermoplastic phase is able to first become molten and then resolidified in order to bind the other components or phases together.

The solid filler phase, on the other hand, will typically comprise a plurality of individual particles or fibers dispersed throughout the thermoplastic phase that themselves will not generally undergo a phase change to form a melt. Instead, the filler phase will remain as a discrete discontinuous solid phase interspersed throughout and among the continuous thermoplastic phase. Although it is possible for the filler to also interact with the thermoplastic phase, the filler will generally not assist in binding the components together. The solid filler phase will typically include discrete particles, such as inorganic particles.

Other discrete phases may include a fibrous phase, comprising either organic or inorganic fibers, an organic filler phase comprising organic particles, and other organic or inorganic materials that may be in any state such as solid, gel, liquid, or gas and which for some reason do not become substantially commingled with the thermoplastic phase so as to be considered part of that phase. Because each of the materials within any of the phases in the thermoplastic starch compositions can be selected to impart a unique property to the overall material, it will be possible to microstructurally engineer a thermoplastic starch material best suited for a particular use based on given performance criteria of e.g., cost, strength, durability, degradability, esthetic appeal, density, flexibility, and the like.

B. Sheets, Films, Containers, and Other Articles Made From Thermoplastics Starch Compositions

The term "sheet" as used in this specification and the appended claims is intended to include any substantially flat,

corrugated, curved, bent, or textured sheet made using the thermoplastic starch compositions and methods described herein. The only essential compositional limitation is that the binding matrix, or thermoplastic phase, comprise starch that has been processed to form a thermoplastic starch melt prior or during the sheet-making process. The sheets may also include organic coatings, printing, other sheets laminated thereto, etc. The sheets within the scope of the present invention can have greatly varying thicknesses depending on the particular applications for which the sheets are intended. The sheets can be as thin as about 0.001 mm or as thick as 1 cm or greater where strength, durability, and or bulk are important considerations.

The term "film" is not inherently differentiating from the term "sheet" except that "film" normally denotes a very thin sheet. Films are often formed by processes that are different from how sheets are normally formed, such as by film blowing rather than sheet calendering. In general, films will be defined as sheet-like articles having thicknesses as low as about 1 micron and up to about 1 mm.

The term "molded article" shall refer to articles that are shaped directly or indirectly from thermoplastic starch compositions using any molding method known in the art for thermoplastic materials. Articles formed by melting and remolding intermediate sheets are also "molded articles" within this definition.

The term "converted article" shall refer to articles that are shaped from sheets, films, or other articles made from thermoplastic starch compositions without a complete remelting step. An example of a "converted article" is a box that is made by cutting, bending, and then gluing a sheet formed from a thermoplastic starch composition of the present invention. Of course, some spot thermoplastic adhesion may be possible to adhere a thermoplastic sheet to itself or another sheet or article without the need to apply a separate adhesive.

The term "container" as used in this specification and the appended claims is intended to include any article, receptacle, or vessel utilized for storing, dispensing, packaging, portioning, or shipping various types of products or objects (including, but not limited to, food and beverage products). Specific examples of such containers are set forth in detail below and include, among others, boxes, cups, "clam shells," jars, bottles, plates, bowls, trays, cartons, cases, crates, cereal boxes, frozen food boxes, milk cartons, bags, sacks, carriers for beverage containers, dishes, egg cartons, lids, straws, envelopes, or other types of holders.

In addition to integrally formed containers, containment products used in conjunction with containers are also intended to be included within the term "container." Such articles include, for example, lids, liners, straws, partitions, wrappers, cushioning materials, utensils, and any other product used in packaging, storing, shipping, portioning, serving, or dispensing an object within a container.

An advantage of the thermoplastic starch compositions of the present invention (as well as containers, films, printed materials, or other articles made therefrom) is that their disposal impacts the environment far less than paper, paperboard, plastic, polystyrene, glass, or metal products. The sheets and articles of the present invention are both readily recyclable and, even if not recycled, will readily degrade and decompose when exposed to moisture, pressure, and other environmental forces into components that are complementary to the components of the earth. The starch component will dissolve slowly in water and will then be quickly degraded by microbial action. Many synthetic polymers are also biodegradable. Organic fillers and fibers

may also be biodegradable and are included in far lesser amounts to begin with compared to paper. The inorganic filler is inert and will be generally compatible with the earth.

II. Phases and Components

A. Thermoplastic Phase

The terms "phase" and "phases", when used in context with the thermoplastic compositions of the present invention, shall refer to the discrete layers or compositional discontinuities within the thermoplastic starch composition. The term "physical state" shall be used to refer to whether a material is a gas, liquid or solid.

The term "thermoplastic phase" is so defined because its plasticity, or ability to flow and be deformed, changes as a function of temperature. When heated sufficiently it flows, and when cooled sufficiently it becomes substantially solidified. The thermoplastic phase will be in a substantially solid state when cooled sufficiently below its melting point or softening range, and in a substantially liquid or semi-liquid state when heated sufficiently above the melting point or softening range. In general, whether the overall thermoplastic starch compositions are plastic or solid will usually be determined by the physical state of the thermoplastic phase and not the other phases dispersed therein. Thus, when the thermoplastic phase is heated to become plastic, the overall thermoplastic starch composition will itself behave in a substantially plastic manner so that it may be shaped into a desired article of manufacture, even though it may contain solid particles or fibers dispersed therein. Similarly, when the thermoplastic phase is thereafter cooled sufficiently so that it becomes resolidified, the overall thermoplastic starch composition will behave as a solid rather than a flowable material, though it is possible for flowable liquids to remain encapsulated within the substantially solidified composition.

In contrast to the thermoplastic phase, the solid phases and optional gaseous phases, dispersed throughout the thermoplastic phase may not themselves undergo any change of physical state change during processing and molding. Nevertheless, because the solid phase and optional gaseous phases are generally disperse phases comprised of discontinuous particles or bubbles, they may generally be considered to be passive constituents within the thermoplastic phase matrix, although these particles and bubbles will often affect the physical and mechanical properties of the thermoplastic starch compositions. Because the solid and optional gaseous phases comprise relatively small particles or spaces within the continuous thermoplastic phase, the overall thermoplastic starch composition can act as either a solid or flowable material on a macro level though it may contain dispersed materials having different physical states on a micro level.

The thermoplastic phase will also act as a binding matrix that will encapsulate the other phases and hold them together when the thermoplastic phases is in a solid state. Nevertheless, it should be understood that the other phases dispersed throughout the thermoplastic phase will often interact with the thermoplastic phase, both mechanically and chemically, in many cases. Some phases may simply act as passive constituents that interrupt the thermoplastic phase, while other phases may actually strengthen the composition by forming mechanical and/or chemical links between different regions of the composition on a macroscopic level. Other phases may primarily affect the density, flexibility, texture, and esthetic appearance of the composition rather than strength. In order to obtain the most beneficial effects from the various phases and components within the thermoplastic starch compositions, one of ordinary skill can select the components within the thermoplastic phase that

will maximize the synergistic effect between the various components in order to provide the best mechanical properties at the least cost. This process of properly selecting components having the best synergistic interaction may be referred to as "microstructural engineering".

The thermoplastic phase will, at a minimum, include starch and a plasticizer that is capable of causing the starch to behave as a thermoplastic material that can form a melt when heated rather than thermally decomposing. The thermoplastic phase may also include one or more additional constituents that can improve the mechanical and/or chemical properties of the thermoplastic phase. In many cases, one or more additional thermoplastic polymers can be added, such as a hydrophobic biodegradable polymer that will make the overall thermoplastic starch composition less sensitive to fluctuations in ambient moisture. In addition, or in lieu of additional polymers, the thermoplastic phase may include substances that chemically react with or physically associate with the starch in order to impart desired properties of e.g., strength and resistance to fluctuations in moisture, such as cross-linking agents, softeners, sealers, phase mediators or humectants. Still other constituents within the thermoplastic phase may simply be solids, liquid, or gases that are dissolved or otherwise mixed throughout the thermoplastic phase in a manner such that they are not thereafter identifiable as a phase that is significantly distinct from the thermoplastic phase.

In the case where the thermoplastic phase includes a synthetic or natural polymer in addition to the thermoplastic starch fraction, the thermoplastic phase will often contain two or more thermoplastic subphases that are preferably substantially homogeneously mixed together but which nevertheless may constitute distinct subphases at the microscopic level. In a mixture of polymers, the polymer chains of one type of polymer will tend to associate with themselves rather than with the polymer chains of another type of polymer. In many cases, the two or more polymers will have varying degrees of hydrophilicity or hydrophobicity, giving them varying degrees of chemical compatibility. Just like water and oil, which are generally immiscible in each other and which tend to separate into distinct phases, so too will more hydrophilic polymers tend to resist blending with more hydrophobic polymers. Nevertheless, just like water and oil, which can be temporarily blended together through vigorous mixing conditions, so too can different polymers be blended together using high shear mixing conditions when heated to become thermoplastic and, hence, Theologically compatible. Upon cooling to resolidify the thermoplastic subphases, the polymers will remain mechanically mixed together in either a solution, as an interpenetrating network of polymeric subphases, or a combination of the two. Whereas water and oil will tend to separate into distinct phases over time, solidification of the blended polymers will, in essence, mechanically interlock the two or more different polymer subphases and prevent them from separating into larger, more distinct subphases.

The thermoplastic phase will generally comprise from about 10% to about 95% by volume of the thermoplastic starch composition, preferably from about 10% to about 90% by volume, more preferably from about 20% to about 80% by volume, and most preferably form about 30% to about 70% by volume. The relative concentrations of the thermoplastic starch and other polymeric subphases will be discussed hereinafter.

1. Starch

The starch component of the thermoplastic phase may comprise any known starch material, including one or more

unmodified starches, modified starches, and starch derivatives. Nevertheless, preferred starches, both from the standpoint of cost and of processability, will include most any unmodified starch that is initially in a native state as a granular solid and which will form a thermoplastic melt by mixing and heating in the presence of an appropriate plasticizer. Starch is a natural carbohydrate chain comprising polymerized glucose molecules in an α -(1,4) linkage and is found in nature in the form of granules. Such granules are easily liberated from the plant materials by known processes. Starch granules include two different types of polymerized glucose chains: unbranched, single-chained amylose and branched multi-chained amylopectin.

In general, starch granules have a coating or outer membrane that encapsulates the more water soluble amylose and amylopectin chains within the interior of the granule. This outer shell makes unmodified native starch granules generally insoluble in water at room temperature. However, when heated in the presence of water or other polar solvent such as glycerin, the solvent is able to soften and penetrate the outer membrane and cause the inner starch chains to absorb water and swell. This swelling will, at some point, cause the outer shell to rupture and allow the irreversible gelatinization or destructure of the starch granule. This process is irreversible because, once gelatinized or destructure, starch can never revert to its native, cold water-resistant, granular state. The exact temperature at which starch will gelatinize in a given plasticizing solvent depends on the type of starch. In general, the higher the amylose content, the higher the gelatinization temperature in water due to the greater insolubility of amylose compared to amylopectin. In the presence of mixing, such as high shear mixing, the rate of melting or destructure is greatly increased.

Once gelatinized or destructure, the various starch polymer chains comprising amylose and amylopectin polymers, which are initially compressed within the granules, will stretch out and form a generally disordered intermingling of polymer chains, particular while in a molten or gelatinized state. Upon resolidification, however, the chains can reorient themselves in a number of different ways in order to form crystalline or amorphous solids having varying strengths depending on the orientation of the starch polymer chains. Orienting, cross-linking, and reacting the polymer chains with other components can greatly affect the resulting physical and mechanical properties of the resolidified starch melt.

Although starch is produced in many plants, an important source are seeds of cereal grains, such as corn, waxy corn, wheat, sorghum, rice, and waxy rice. Another important source includes tubers, such as potatoes, roots such as tapioca (i.e., cassava and manioc), sweet potato, and arrowroot, and the pith of the sago palm. In general, potato and waxy corn starches are generally higher in amylopectin, while corn and rice starches are generally higher in amylose. Depending on the desired properties of the final thermoplastic starch composition, one may select the type of starch that will give the most desired benefits, both in terms of cost and final physical, mechanical and strength properties.

The concentration of starch within the thermoplastic phase can vary greatly depending on whether or not other constituents are added the thermoplastic phase. Because starch is not by itself a thermoplastic material but must be admixed with one or more plasticizers, the concentration of thermoplastic starch within the thermoplastic phase will be understood to include a mixture of starch and plasticizer. Thus, if the thermoplastic phase were to contain 100% of a starch melt, the actual concentration of molecular starch

would be less than 100%, with the balance comprising the plasticizer, as well as optional components, such as cross-linking agents, blocking groups, substitution groups, and the like. Because of the difficulty in sorting out the exact identities and concentrations of these other nonstarch constituents, particularly after they have interacted with the starch molecules, the starch, plasticizers, and other constituents added to react with the starch will be referred to in the aggregate as comprising the "starch melt" fraction or component.

In some cases, as will be discussed more fully in the section relating to preferred methods of forming starch melts, it may be particularly advantageous to use starch that has been predried to remove some or substantially all of the water that is naturally associated with native starches. In general, native unmodified starch granules will include from about 10–20% water by weight. Because this water can have a variety of possibly negative effects during the formation of starch melts, for example when it is desired to react the starch with another constituent by means of a condensation reaction, it may be advantageous to remove this water before mixing and heating the starch with the plasticizer to form a melt, or at least before reacting the starch melt with the other constituent. In those cases where it may be desirable to pre-dry the starch while in a native granular state, it will be preferable to reduce the water content to below about 10% by weight of the starch granules, more preferably to below about 5% by weight, and most preferably to below about 3% by weight.

In other cases, it may be adequate to simply remove a substantial portion of the water from the starch melt by evaporation by means of a venting or degassing during processing, preferably to concentration of less than about 5% by weight of the starch, more preferably to below about 3% by weight, and most preferably to below about 1% by weight before cooling and resolidification. Venting or degassing can also be employed to remove reaction water that may be produced within the thermoplastic phase by, e.g., condensation reactions between starch and one or more synthetic polymers, acids, acid halides or anhydrides, or other admixtures. Where an extremely low amount of water will remain within the thermoplastic starch melt after venting, it will generally be necessary to include one or more low volatile plasticizers so as to maintain the starch as a melt as the water is released. As such, the low volatile plasticizers will "replace" the water normally associated with starch.

In some cases, it may be preferable for the thermoplastic phase to include 100% of the "starch melt", as that term has been defined above. In those instances where an additional thermoplastic polymer is included, the starch melt will preferably have a concentration in a range from about 10% to about 90% by weight of the thermoplastic phase, more preferably in a range from about 20% to about 80% by weight, and most preferably in a range from about 30% to about 70% by weight.

2. Plasticizers

In manufacturing thermoplastically processible starch melts, there have been essentially two alternative approaches that utilize what may be considered to be two different plasticizing or melt initiating systems. For simplicity, these two alternative approaches may be referred to as "destructure starch" and "thermoplastic starch", although other terms have been used in the art. The term "destructure starch" has typically been used when referring to processes for forming a starch melt in which the starch granules are made thermoplastic by heating and mixing the starch in the presence of water under carefully

controlled conditions of temperature, pressure and concentration. Because water is generally volatile at the temperatures necessary to form a starch melt, the destructure-
 5 process must generally take place within a closed vessel capable of preventing the escape of water by evaporation so as to maintain the desired concentration of water throughout the manufacturing process. By maintaining a constant water concentration within the closed vessel, it is possible to form starch melts in which the water acts as the primary or sole,
 10 plasticizing solvent. Upon cooling to below the melting or softening point or range, the destructure starch melt resolidifies as a thermoplastic material.

Gelatinizing or destructure starch in any quantity of water will not always yield a starch material that will act as a thermoplastic material, but only where sufficiently low
 15 water is used so that the resulting melting point or softening range is sufficiently higher than room temperature so as to reliably form a solidified product upon cooling. If too much water is used, the gelatinized starch can only be solidified by evaporating away a substantial portion of the water in order
 20 to either raise the melting point or softening range sufficiently or in order to dry it to the point of recrystallization so that it solidifies while being heated rather than after being cooled.

In order for "destructure starch" to behave as a thermoplastic material that will solidify as a result of cooling
 25 sufficiently below its melting or softening point, it will generally be necessary for the water to be included in a range from about 5% to about 4% by weight of the starch (including the water naturally found in native starch). If
 30 more than about 40% is included, the melting point or range will usually be too low for the starch/water mixture to reliably solidify within a reasonable period of time when cooled. If the water is not maintained above about 5%
 35 throughout processing, and absent the inclusion of another plasticizer such as glycerin, the starch will usually not form or be maintained as a melt at a temperature sufficiently lower than the decomposition temperature of starch, which is about 230–250° C.

One problem with using water as a melt initiation agent is
 40 that it may, in some cases, inhibit desired chemical reactions between the starch melt and other additives, unless removed by evaporation prior to the occurrence of such reactions. The reactive additive may be a nonpolymeric reagent, or it may
 45 comprise one or more thermoplastic polymers that have reactive groups that can react with, e.g., the hydroxyl groups of the starch polymer. For example, it may be desirable to reduce the hydrophobicity of the starch polymer by reacting
 50 or otherwise blocking the hydroxyl groups such as by esterification, etherification, or other condensation reaction, or by substitution, elimination, or formation of acetal or ketal groups. Because water is a byproduct of condensation
 55 reactions, its presence within the starch melt may inhibit or even prevent such reactions. Water may also compete as a reactant with the starch in some cases.

Certain polymers may also experience degradation or partial cleavage of the polymer chain when heated in the
 60 presence of water. For example, it is known that many polyesters can experience chain degradation and reduction of molecular weight through hydrolysis reactions with water at elevated temperatures. Reducing the molecular weight of
 65 polymers tends to weaken films and other articles made therefrom. Although not known for sure, it may be possible for water to degrade or hydrolyze a significant proportion of the acetal linkages within starch molecules at elevated temperature, particularly under high shear conditions, which may reduce the molecular weight of the starch molecules to

some extent. Thus, in order to prevent hydrolysis of polymer linkages within one or polymers within a thermoplastic
 starch melt, it may be preferable to limit the length of time that certain polymers are exposed to substantial moisture at
 5 elevated temperatures.

Destructurized starch may also tend to form retrograde starch over time as a result of moisture loss. Retrograde starch is much more brittle and less flexible compared to thermoplastic starch compositions having lower crystallinity. When destructure starch melts are initially formed,
 10 the water is able to interact with the hydroxyl groups of the starch molecules in order to interrupt the starch molecules and keep them from associating themselves into a more crystalline geometry. However, in normal ambient conditions the water within destructure starch is free to migrate into and out of the destructure starch over time, thus
 15 compromising the ability of the water to prevent crystallization and retrogradation of the destructure starch.

In view of the volatile nature of water and also the tendency of water to inhibit certain desired chemical reactions or hydrolyze certain polymers, another approach to making a starch melt is to substitute some or all of the water with less volatile plasticizers (e.g., glycerin) or even higher
 20 molecular weight plasticizers that are essentially nonvolatile. For simplicity, less volatile and nonvolatile plasticizers or solvents that have a vapor pressure of less than 1 bar at the melting temperature of the starch melt shall be collectively referred to as "low volatile" plasticizers for purposes of this disclosure. Conversely, melt initiators comprising
 25 volatile solvents (e.g., water, alcohols, amines, aldehydes, ketones, organic acids, esters, amides, imides, and the like) that have a vapor pressure of 1 bar or greater at the melting temperature of the starch melt will be considered to "volatile" melt initiators or solvents. In the past, some have referred to starch melts that use low volatile plasticizers instead of water as "thermoplastic starch". On the other
 30 hand, starch that has been melted in the presence of water has been referred to as "destructure starch". Nevertheless, for purposes of the present invention, the terms "thermoplastic starch", "thermoplastic starch composition" and "thermoplastically processible starch" shall be understood to include compositions that include both low volatile and
 35 volatile plasticizers to form the starch melt.

Although not an exhaustive list, examples of preferred low volatile plasticizers that can be used alone or together in various mixtures to make the thermoplastic starch compositions within the scope of the present invention include ethylene glycol, propylene glycol, glycerin, 1,3-propanediol, 1,2-butandiol, 1,3-butandiol, 1,4-butanediol, 1,5-pentandiol, 1,5-hexandiol, 1,6-hexandiol, 1,2,6-hexantriol, 1,3,5-hexantriol, neopentylglycol, sorbitol acetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate, sorbitol hexaethoxylate, sorbitol dipropoxylate, aminosorbitol, trihydroxymethylaminomethane, glucose/PEG, the reaction
 40 product of ethylene oxide with glucose, trimethylolpropane monoethoxylate, mannitol monoacetate, mannitol monoethoxylate, butyl glucoside, glucose monoethoxylate, α -methyl glucoside, the sodium salt of carboxymethylsorbitol, polyglycerol monoethoxylate, erythritol, pentaerythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol, allitol, sorbitol, polyhydric alcohols generally, esters of glycerin, formamide, N-methylformamide, DMSO, mono- and diglycerides, alkylamides, polyols, trimethylolpropane, polyvinylalcohol with from 3 to 20 repeating units, polyglycerols with from
 45 2 to 10 repeating units, and derivatives of the foregoing.

Examples of derivatives include ethers, thioethers, inorganic and organic esters, acetals, oxidation products, amides, and amines.

In general, more preferred plasticizers will have a solubility parameter of at least about $15 \text{ kg}^{1/2}\text{cm}^{-3/2}$ within a temperature range of about $150\text{--}300^\circ \text{C}$., and most preferably in a range from about $15 \text{ kg}^{1/2}\text{cm}^{-3/2}$ to about $25 \text{ kg}^{1/2}\text{cm}^{-3/2}$. Such plasticizers can be blended with a wide variety of other co-solvents or plasticizers both within and without the preferred solubility parameter ranges.

The concentration of low volatile plasticizer that is used may vary greatly depending on the type of starch and plasticizer being used, as well as on the identity and concentration of other possible components within the thermoplastic phase. In some cases it may be desirable to use a mixture of different plasticizers in order to impart specifically engineered properties into both the starch melt and final thermoplastic starch composition. In general, the low volatile plasticizer will have a concentration in range from about 1% to about 70% by weight of the starch, more preferably in a range from about 5% to about 50% by weight, and most preferably in range from about 10% to about 30% by weight.

Low volatile plasticizers yield thermoplastic starch compositions that tend to remain more stable, more flexible, less crystalline, and less brittle over time compared to destructured starch. They do this by keeping the starch more amorphous over time. Unlike water, which can readily migrate into and out of destructured starch by evaporation under ambient conditions to form crystalline starch, low volatile plasticizers tend to remain more closely associated with the hydroxyl groups of the starch molecules over time. Thus, by remaining interposed between the various starch polymer chains within the composition, the plasticizer can better inhibit recrystallization and retrogradation of the starch chains compared to water or other more volatile plasticizers.

Nevertheless, some "low volatile" plasticizers have a vapor pressure that allows for significant, albeit more slow, evaporation from solidified starch melts. Such evaporation may be more pronounced when an article made from a thermoplastic starch composition is exposed to heat. An example of a low volatile plasticizer that nevertheless has a significant vapor pressure is glycerin. In the case where a low volatile plasticizer may tend to evaporate or otherwise migrate out of the thermoplastic starch composition over time, it may be preferable in some cases to also include a higher molecular weight plasticizer that has a much lower vapor pressure in order to inhibit migration and loss of the higher vapor pressure, low volatile plasticizer from the solidified thermoplastic starch composition. Moreover, because some higher molecular weight plasticizers are in a solid state at room temperature, they may remain more firmly embedded within thermoplastic starch compositions at room temperature compared to plasticizers that are liquid at room temperature. An example of a higher molecular weight plasticizer that has a much lower vapor pressure than glycerin and which is a solid at room temperature is sorbitol.

Moreover, in those cases where the thermoplastic starch melt is exposed to a venting process in order to remove unwanted water vapor prior to shaping, it may be necessary to account for the possibility that a portion of a low volatile plasticizer having a significant vapor pressure at the melt temperature may also be removed by evaporation as a result of the venting process. The formation of azeotropes with water and/or steam distillation of low volatile or even nonvolatile plasticizers by water can further increase the rate of loss of low volatile plasticizers during venting. Of course,

maintaining lower water, or even eliminating water altogether, can reduce or prevent loss of the low volatile plasticizer.

3. Additional Polymers

In many cases it may be desirable to include one or more additional polymers within the thermoplastic phase in order to improve the properties of the resulting thermoplastic starch composition. Both synthetic and natural polymers may be included within the thermoplastic phase. Such polymers may improve the processability of the starch melts, although their major contribution will typically be to improve the mechanical and/or chemical properties of the final hardened thermoplastic starch composition. For example, more hydrophobic polymers may be used to decrease the sensitivity of the final thermoplastic starch composition to changes in ambient moisture and/or to make the material more water insoluble or impermeable.

Depending on its chemical nature and, to some extent, the process and type of plasticizer being used, the additional thermoplastic polymer may or may not actually chemically interact with the thermoplastic starch subphase. Although virtually any thermoplastic polymer can be mixed with the thermoplastic starch subphase to some extent to form a blend intermixed thermoplastic subphases, the thermoplastic phase will exhibit more uniform mechanical properties where the starch and other thermoplastic polymer are more homogeneously intermixed. It has been found that the most homogeneous blending of starch and other polymer occurs where at least a portion of the starch and other polymer are chemically linked together, such as by a condensation reaction or some other chemical linking reaction. It would be ideal if substantially all of the starch were to become chemically linked with the other polymer(s). In many cases, however, only a portion of the starch will be able to react with the other polymer(s). In such a case, it has been found that the portion of the starch that reacts with the other polymer(s) will advantageously form a hybrid polymer that acts as a compatibilization subphase or phase mediator that yields a more homogeneously blended mixture of the unreacted phases of starch and other polymer(s). It should be understood, however, that the present invention is not limited by the extent to which the starch and other polymer may or may not chemically interact. A wide variety of polymers that do not react with starch may be used within the scope of the invention.

Examples of preferred biodegradable synthetic thermoplastic polymers that may be blended with the thermoplastic starch phase include, but are not limited to:

- (a) homopolymers of aliphatic and aromatic hydroxyacid monomers and their corresponding lactones or lactides;
- (b) copolymers of a first monomer of group (a) and second monomer selected from the group consisting of (1) a monomer of group (a) different from the first monomer and (2) aliphatic or aromatic isocyanates;
- (c) block or graft copolymers between the homopolymers and copolymers of groups (a) or (b) and one or more of the following components:
 - (i) cellulose or cellulose derivatives such as cellulose acetate, cellulosic ethers, and carboxymethylcellulose;
 - (ii) amylose, amylopectin, natural starch, or modified starches;
 - (iii) polymers derived from reaction of diols (such as ethylene glycol, propylene glycol, butylene glycol, polyoxyethylene glycol, polyoxypropylene glycol, neopentyl glycol, 1,4-butanediol, cyclohexandiol, or dianhydrous sorbitol), polyester prepolymers, or polymers having diol terminal groups with:

aromatic or aliphatic bifunctional isocyanates or epoxides,

aliphatic bicarboxylic acids (such as malonic, succinic, maleic, fumaric, itaconic, glutaric, adipic, pimelic, suberic, azelaic, or sebacic acids),
 bicarboxylic cycloaliphatic acids (such as cyclohexane bicarboxylic acids or 2,2,2-bicyclooctane bicarboxylic acid), or aromatic acids or anhydrides (such as phthalic acid);

(iv) polyurethanes, polyamide-urethanes from diisocyanates and aminoalcohols, polyamides, polyester-amides from bicarboxylic acids and aminoalcohols, polyester-urea from aminoacids and diesters of glycols,

(v) polyhydroxylated polymers (such as polyvinylalcohol), ethylene-vinylalcohol copolymers, totally or partially hydrolyzed, and polysaccharides;

(vi) polyvinylpyrrolidone, polyvinylpyrrolidonevinylacetate copolymers, polymethacrylates;

(d) polyesters obtained from monomers or comonomers such as defined above in (a) and (b) upgraded with chain extenders, such as isocyanates, epoxides, phenylesters and aliphatic carbonates; and

(e) polyesters obtained from monomers and comonomers defined above in (a) and (b) partially cross-linked by means of polyfunctional acids such as trimellitic acid, pyromellitic acid, polyisocyanates and polyepoxides.

As monomers of aliphatic hydroxyacids having from 2 to 24 carbon atoms, the following acids and corresponding lactides or lactones may be used:

α-hydroxyacids such as lactic acids and the corresponding lactide, glycolic acid and the corresponding glycolide;

β-hydroxyacids such as hydroxypropionic acid, hydroxyvaleric acid and hydroxypelargonic acid and the corresponding lactone;

γ-hydroxyacids such as hydroxybutyric and the corresponding lactone;

δ-hydroxyacids such as hydroxyvaleric acid and the corresponding lactone;

ε-hydroxyacids;

hydroxyacids having the hydroxy group placed beyond the 6-position such as 10-hydroxydecanoic acid; products of natural origin such as sabinic acid (12-hydroxydodecanoic) and juniperic acid (16-hydroxyhexadecanoic); unsaturated hydroxyacids such as ricinoleic acid; acids deriving from alpha-hydroxylation of fatty acids such as myristic, palmitic and stearic acids; acids deriving from hydroxylation of unsaturated fatty acids such as oleic, ricinoleic, linolenic and erucic acids;

cycloaliphatic hydroxyacids such as the hydroxyacids of cyclohexane and of 2,2,2-bicyclooctane.

Homopolymers and copolymers of ε-hydroxyacids are preferred, particularly of 6-hydroxycaproic acid, 6-hydroxyoctanoic, 3,7-dimethyl-6-hydroxyoctanoic acid and corresponding lactones, such as poly-ε-caprolactone.

As copolymers of aliphatic hydroxyacids with isocyanates, copolymers of epsilon-caprolactone with 4,4'-diphenylmethane-diisocyanate (MDI), tolylenediisocyanate (TDI), isophoron diisocyanate or hexanmethylenediisocyanate are preferred.

As the copolymers of aliphatic hydroxyacids and the corresponding lactones with aromatic hydroxyacids/ copolymers of ε-caprolactone with β-phenyl lactic acid or mandelic acid are preferred.

Another class of useful polyesters are the so-called "aliphatic-aromatic copolyesters" which have superior mechanical and physical properties by virtue of the aromatic portion, as well as good biodegradability as a result of the aliphatic portion. Examples of useful aliphatic-aromatic copolyesters that may be blended within the thermoplastic starch compositions of the present invention include, but are not limited to, polyesters described in U.S. Pat. No. 5,292,783 to Buchanan et al., U.S. Pat. No. 5,446,079 to Buchanan et al., U.S. Pat. No. 5,559,171 to Buchanan et al., U.S. Pat. No. 5,580,911 to Buchanan et al., U.S. Pat. No. 5,599,858 to Buchanan et al., U.S. Pat. No. 5,900,322 to Buchanan et al., and U.S. Pat. No. 5,817,721 to Warzelhan et al. For purposes of disclosing exemplary aliphatic-aromatic copolyesters that may be used to form the inventive starch based compositions of the present invention, the foregoing patents are incorporated herein by specific reference. A presently useful aliphatic-aromatic copolyester is 1,4-butandioladipinic acid and teraphthalic acid with a chain extender comprising isocyanate.

The foregoing polymers are preferred because they have been found to form good thermoplastic blends of starch having good biodegradability and good mechanical and chemical properties. In addition, the foregoing polymers comprise polyesters that are capable of cross esterifying with starch, especially where little or no water is used. Besides the foregoing, virtually any synthetic or natural polymer that can form a cross esterification or other condensation reaction with the hydroxyl groups on the starch polymers are within the scope of the present invention. In fact, any polymer that can react with the starch will be preferred since the resulting starch/polymer blends will be chemically interlinked together and thus more homogeneous.

Nevertheless, there is a huge variety of other polymers that may or may not react with the starch but that nevertheless may be utilized within the scope of the present invention. These include polyolefines, alkylsiloxanes, polyesteramides, polyethers, polyethylene adipate (PEA), polytetramethylene adipate and the like aliphatic polyesters and their derivatives, cycloaliphatic polyesters and their derivatives, copolymers derived from a thermoplastic synthetic resin and a biodecomposable aliphatic polyester, polyethylene, polypropylene, ethylene-vinylacetate copolymer and its saponified products, polyester resins such as polyethylene terephthalate (PET), polybutylene terephthalate, vinyl resins such as polyvinyl chloride, polyvinylidene acetate, polystyrene and styrene copolymers, polyamide resins, polycarbonate resins, cellulosic esters (e.g., cellulose formate, cellulose acetate, cellulose diacetate, cellulose propionate, cellulose butyrate, cellulose valerate, and mixtures of the foregoing), ethylene acrylate maleic acid and hydride terpolymer, polyacrylic acids, polycaprolactone/polyvinyl alcohol block copolymer, polysaccharides that have been chemically modified to contain added hydroxyalkyl groups, copolymers of vinyl pyrrolidone, polyalkyleneimine polymers and copolymers, styrene-sulfonic acid polymers, copolymers and salts thereof, and virtually any polymer that can be thermoplastically processed at a temperature that would allow it to be blended with the thermoplastic starch subphase.

Examples of preferred natural polymers or polymers derived from natural materials that can be blended into thermoplastic starch melts include a wide variety of cellulosic materials, proteins, and polysaccharide materials such as gums. Because cellulose is chemically similar to starch, cellulose based materials will have a greater affinity for

starch compared to most other materials. One class of cellulose derived materials includes the cellulosic ethers, examples of which include methylhydroxyethylcellulose, hydroxymethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxyethylpropylcellulose, and the like, as well as mixtures or derivatives thereof. Another class of cellulose derivatives are esters of cellulose, such as cellulose acetate, cellulose diacetate, cellulose formate, cellulose propionate, cellulose butyrate, mixed esters, and the like.

Other polysaccharide-based polymers that can be incorporated into starch melts include alginic acid, alginates, phycocolloids, agar, gum arabic, guar gum, acacia gum, carrageenan gum, furcellaran gum, ghatti gum, psyllium gum, quince gum, tamarind gum, locust bean gum, gum karaya, xanthan gum, and gum tragacanth, and mixtures or derivatives thereof.

Suitable protein-based polymers include, for example, Zein® (a prolamine derived from corn), collagen (extracted from animal connective tissue and bones) and derivatives thereof such as gelatin and glue, casein (the principle protein in cow milk), sunflower protein, egg protein, soybean protein, vegetable gelatins, gluten and mixtures or derivatives thereof.

Although it will be preferable in many cases to reduce the water content of the thermoplastic phase, it is nevertheless within the scope of the invention to use water as a significant portion of the plasticizer. In the case where it is not critical to reduce or eliminate water altogether, it may be advantageous to include one or more water-dispersible polymers. Examples of water-dispersible polymers that may be used in both the presence or absence of water include polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol, polyvinylmethyl ether, polyacrylic acids, polyacrylic acid salts, polyvinyl acrylic acids, polyvinyl acrylic acid salts, polyacrylimides, ethylene oxide polymers, polylactic acid, latex (which is a broad category that includes a variety of polymerizable substances formed in a water emulsion, an example of which is styrene-butadiene copolymer), and mixtures or derivatives thereof.

As mentioned above, some polymers such as polyesters or other polycondensates may degrade or undergo chain shortening by hydrolysis if exposed to water at elevated temperature. Although replacing some or all of the water with a different plasticizer may reduce or prevent hydrolysis, some polymers such as polyesters can absorb significant amounts of moisture from the air. In such cases, it may be necessary to subject such polymers to a predrying step in order to prevent subsequent breakdown during thermal processing. Nevertheless, some degree of chain shortening may be desirable since it will increase the number of hydroxyl sites available for subsequent condensation with hydroxyl groups of the thermoplastic starch subphase.

In those instances where one or more additional thermoplastic polymers are included within the thermoplastic phase, the one or more polymers will, in the aggregate, preferably have a concentration in a range from about 10% to about 90% by weight of the thermoplastic phase, more preferably in a range from about 20% to about 80% by weight, and most preferably in a range from about 30% to about 70% by weight.

4. Other Additives

In addition to the basic components of starch, plasticizer and optional natural and synthetic polymers, other liquids, solids, or gases may be considered to be part of the thermoplastic phase.

It may also be possible to add a reactive agent that in addition to, or instead of, the additional thermoplastic poly-

mer can improve the properties of the thermoplastic starch material. Such reactive agents may include, but are not limited to, cross-linking agents, used to cross link the starch molecules with either other starch molecules or the one or more additional thermoplastic polymers, reagents that add additional functional groups to the starch or additional polymer, reagents that may serve to block the hydroxyl functional groups on the starch polymers, and reagents that serve to form a phase mediator. Examples of the foregoing include monovalent, divalent, and polyvalent carboxylic acids, as well as their anhydrides, acid halides, and acid amides, epoxides, formaldehyde and/or urea and their derivatives, divinyl sulfones, isocyanates, oxo compounds such as acetone formaldehyde or polyvalent oxo compounds, cyanamide, dialdehydes, methylureas, and melamineformaldehyde resins.

In the case where it is desired for the starch to form an ester with another thermoplastic polymer, it may be helpful, in addition to eliminating most or all of the water, to employ an esterification catalyst or promoter. For example, the esterification reaction between thermoplastic starch and polyesters, such as polycaprolactone or aliphatic-aromatic copolyesters, can be facilitated by $Ti(OR)_4$, where R is an appropriate alkyl or aryl unit. However, because $Ti(OR)_4$ will hydrolyze in the presence of water, it will be preferable to eliminate most or all of the water in the case where $Ti(OR)_4$ is used.

In addition, nonreactive additives such as humectants (e.g., silica gel and zeolites), dispersants, lubricants (e.g., lipids or metal stearates), softeners, mold release agents (e.g., metal stearates), flexibilizers, and blending enhancers can be added.

B. Solid Phases

1. Inorganic Particulate Fillers

Besides the thermoplastic phase, the other required phase within the thermoplastic starch compositions of the present invention is the filler phase, which may include an inorganic particulate filler. In general, this phase will comprise a plurality of individual filler particles. In many cases the inorganic fillers within the scope of the present invention will be substantially inert and unreactive and, as such, will constitute a passive filler that does not contribute any additional binding or bonding activity. Filler particles that are capable of chemically bonding, interacting or otherwise associating with the starch and other components in the thermoplastic phase are certainly within the scope of the present invention, however. The term "particle" should be interpreted broadly to include filler particles having any of a variety of different shapes and aspect ratios. Both spheroids and flakes are examples of "particles" as that term is defined. In general, however, particles having an aspect ratio (i.e., the ratio of length to thickness) greater than about 10:1 may be better understood as constituting a "fiber" as that term will be defined and discussed hereinbelow.

Virtually any known filler, whether inert or reactive, can be incorporated into the thermoplastic starch compositions of the invention. In general, adding an inorganic filler will tend to greatly reduce the cost of the resulting thermoplastic starch composition. If a relatively small amount of inorganic filler is used, the effects on the strength of the final composition are minimized, while adding a relatively large amount of inorganic filler will tend to maximize those effects. In those cases where adding the inorganic filler will tend to detract from a critical physical parameter, such as tensile strength or flexibility, only so much of the filler should be added in order to reduce the cost of the resulting composition while retaining adequate mechanical properties required

by the intended use. However, in those cases where adding the inorganic filler will improve one or more desired physical properties of a given application, such as stiffness and compressive strength, it may be desirable to maximize the quantity of added filler in order to provide this desired property while also proving greatly decreased cost.

Because different types of inorganic fillers may impart different properties to the final thermoplastic starch composition, two or more fillers may be included that can impart these varying and desired properties. It can be readily appreciated that one of ordinary skill in the art, using a microstructural engineering approach, can select the types and amount of the various inorganic fillers that may be included within the thermoplastic starch composition in order to engineer a final material having the desired strength properties while taking advantage of the cost-reducing properties of adding the inorganic filler. Of course, even if cost is not a factor, or if the addition of an inorganic filler does not appreciably decrease the cost, adding a significant quantity of an inorganic filler as taught herein for any reason is certainly within the scope of the invention.

In general, in order to maximize the quantity of inorganic filler while minimizing the deleterious mechanical effects of adding the filler as much as possible, it will generally be preferable to select filler particles in a manner that decreases the specific surface area of the particles. The specific surface area is defined as the ratio of the total particle surface area versus the total particle volume. One way to decrease the specific surface area is to select particles that have a more uniform surface geometry. The more jagged and irregular the particle surface geometry, the greater will be the ratio of surface area to volume of that particle. Another way to decrease the specific surface area is to increase the particle size.

Particles that have decreased surface area generally require less of the thermoplastic phase for lubrication in order to provide a desired rheology during mixing and molding. Particles having decreased specific surface area also require less thermoplastic material for subsequent binding. Conversely, particles having increased surface area per unit volume of particles will generally require more of the thermoplastic phase for lubrication during shaping and subsequent binding. Hence, all things being equal, decreasing the specific surface area of the filler particles allows more of the filler to be used while maintaining desired mixture rheology while in a thermoplastic melt state. Similar, decreasing the specific surface area of the filler particles allow more of the filler to be used while maintaining desired final strength properties.

In view of the advantages of decreasing the specific surface area of the inorganic filler, it will be preferable to include inorganic filler particles having a specific surface area in a range from about 0.1 m²/g to about 400 m²/g, more preferably in range from about 0.15 m²/g to about 50 m²/g, and most preferably in a range from about 0.2 m²/g to about 2 m²/g.

Related to decreased specific surface area in improving the rheology and final strength properties of the thermoplastic starch compositions of the present invention is the concept of particle packing. Particle packing relates to the use of differently sized and graded filler particles that are selected in order for the particles to more completely fill the interstitial spaces between the particles. In general, the spaces between the particles will be occupied by a corresponding quantity of the thermoplastic phase. To be sure, a certain minimum amount of thermoplastic phase material will always be required to adequately lubricate the particles

during the shaping process and in order to subsequently bind the particles together. Nevertheless, poorly packed filler particles having excess interstitial space therebetween will require more of the thermoplastic phase to occupy the interstitial space while not providing any additional lubricating and binding activity.

Since both the actions of lubrication and the binding of particles are generally limited to regions immediately surrounding the particles, there is, for any given system of inorganic filler particles and thermoplastic phase a "lubrication zone" and "binding zone". Within the "lubrication zone", the thermoplastic polymer melt is able to impart most if not all of its inherent lubrication activity. Thus, any thermoplastic polymer melt located outside this lubrication zone will constitute excess thermoplastic polymer so far as the operation of lubrication is concerned. Likewise, resolidified thermoplastic polymer located within the "binding zone" will impart most of its inherent binding activity, while polymer located outside the binding zone will constitute excess thermoplastic polymer so far as the binding function is concerned. Thus, it can be readily seen that thermoplastic polymer that is located outside of both the lubrication and binding zones may be considered to be excessive and wasteful in those cases where it is desired to maximize the inorganic filler content and thereby minimize the thermoplastic polymer content.

In order to reduce the amount of thermoplastic polymer phase required to impart a given amount of lubrication and subsequent binding, it will be advantageous to select particles that will pack together in a manner that reduces the interstitial space between the particles, particularly the "wasted" space that would otherwise be occupied by the thermoplastic phase. Particle packing techniques allow for a reduction in wasted interstitial space while maintaining adequate particle lubrication and, hence, mixture rheology, while also allowing for more efficient use of the thermoplastic phase as a binder in the final hardened thermoplastic starch compositions of the present invention. Simply stated, particle packing is the process of selecting two or more ranges of particle sizes in order that the spaces between a group of larger particles is substantially occupied by a selected group of smaller particles. In this manner, it is possible to select differently sized particles that maintain sufficient interstitial space to provide the aforementioned lubrication and binding zones, while reducing the volume of "wasted" space between the lubrication and binding zones that must otherwise be occupied by the thermoplastic phase. Eliminating the "wasted" space by filling these spaces with inorganic filler particles allows for the inclusion of more filler while maintaining the desired level of particle lubrication during shaping and particle binding upon solidification the thermoplastic phase.

In order to optimize the packing density of the inorganic filler particles, differently sized particles having sizes ranging from as small as about 0.01 micron to as large as about 2 mm may be used. Of course, the thickness and other physical parameters of the desired article to be manufactured from any given thermoplastic starch composition may often dictate the upper particle size limit. In general, the particle packing will be increased whenever any given set of particles is mixed with another set of particles having a particle size (i.e., width and/or length) that is at least about 2 times bigger or smaller than the first group of particles. The particle packing density for a two-particle system will be maximized whenever the size ratio of a given set of particles is from about 3–10 times the size of another set of particles. Of course, three or more different sets of particles may be used to further increase the particle packing density.

The degree of packing density that will be "optimal" will depend on a number of factors including, but not limited to, the types and concentrations of the various components within both the thermoplastic phase, the inorganic filler phase, and other optional phases, the shaping method that will be employed, and the desired mechanical and other performance properties of the final articles to be manufactured from a given thermoplastic starch composition. One of ordinary skill in the art will know the level of particle packing that will optimize the packing density by practicing the invention described herein.

A more detailed discussion of particle packing techniques can be found in U.S. Pat. No. 5,527,387 to Andersen et al., as well as the following article coauthored by one of the inventors of the present invention: Johansen, V. & Andersen, P. J., "Particle Packing and Concrete Properties," *Materials Science of Concrete II* at 111-147, The American Ceramic Society (1991). Further information relating to particle packing techniques is available in the Doctoral Dissertation of Andersen, P. J., "Control and Monitoring of Concrete Production—A Study of Particle Packing and Rheology," The Danish Academy of Technical Sciences. For purposes of disclosing particle packing techniques useful in practicing the present invention, the foregoing patent, article and doctoral dissertation are incorporated herein by specific reference.

In those cases where it is desired to take advantage of the improved properties of rheology and binding efficiency utilizing particle packing techniques, it will be preferable to include inorganic filler particles having a particle packing density in a range from about 0.5 to about 0.95, more preferably in range from about 0.6 to about 0.9, and most preferably in a range from about 0.7 to about 0.8.

Examples of use full inorganic fillers that may be included within the thermoplastic starch compositions of the present invention include such disparate materials as sand, gravel, crushed rock, bauxite, granite, limestone, sandstone, glass beads, aerogels, xerogels, mica, clay, synthetic clay, alumina, silica, fly ash, fumed silica, fused silica, tabular alumina, kaolin, microspheres, hollow glass spheres, porous ceramic spheres, gypsum dihydrate, insoluble salts, calcium carbonate, magnesium carbonate, calcium hydroxide, calcium aluminate, magnesium carbonate, titanium dioxide, talc, ceramic materials, pozzolanic materials, salts, zirconium compounds, xonotlite (a crystalline calcium silicate gel), lightweight expanded clays, perlite, vermiculite, hydrated or unhydrated hydraulic cement particles, pumice, zeolites, exfoliated rock, ores, minerals, and other geologic materials.

Different inorganic fillers will impart their own unique surface characteristics to the composition and may be chosen accordingly. For example, kaolin gives a smoother, less porous finish, while plate-like materials such as mica and other clays yield a shiny surface. Typically, larger filler particles produce a matte surface, while smaller particles produce a glass-like surface. Substantially transparent fillers such as glass beads or spheres can be used to yield a substantially transparent or translucent thermoplastic starch composition.

Hydraulic cement, gypsum hemihydrate and other hydraulically reactive materials are particularly useful filler materials because of their ready availability, extreme low cost, and because they can be used, if desired, to scavenge excess water that might be present within the thermoplastic starch material, thereby eliminating, or at least reducing, the aforementioned deleterious effects of water.

A wide variety of other inorganic fillers may be added to the thermoplastic starch compositions within the scope of

the present invention, including materials such as metals and metal alloys (e.g., stainless steel, iron, and copper), balls or hollow spherical materials (such as glass, polymers, and metals), filings, pellets, flakes and powders (such as microsilica).

Another class of inorganic fillers that may be added to the thermoplastic starch compositions includes inorganic gels and microgels such as silica gel, calcium silicate gel, aluminum silicate gel, and the like. These can be added in solid form or may be precipitated in situ. Since gels and microgels tend to absorb water, they can be added to reduce the negative effects of water within the thermoplastic starch compositions during processing, thereby increasing the ability of starch to react with given reagents and thermoplastic polymers. In addition, the highly hygroscopic nature of silica-based gels and microgels allows them to be used as moisture scavengers within the final hardened thermoplastic starch compositions. By preferentially absorbing moisture from the air, the gels and microgels can reduce moisture sensitivity of the thermoplastic starch compositions, particularly when exposed to high humidity, which can cause solidify starch melts to soften. Controlling the moisture content of the thermoplastic starch compositions allows for more careful control of the elongation, toughness, modulus of elasticity, bendability, foldability, flexibility, and ductility of articles manufactured therefrom. Zeolites can also be added to preferentially absorb moisture in order to reduce the negative effects of moisture in thermoplastic starch compositions.

The particle size or range of particle sizes of the inorganic fillers will depend on the wall thickness of the film, sheet, or other article that is to be manufactured from the thermoplastic starch composition. In general, the larger the wall thickness, the larger will be the acceptable particle size. In most cases, it will be preferable to maximize the particle size within the acceptable range of particle sizes for a given application in order to reduce the cost and specific surface area of the inorganic filler. For films that are intended to have a substantial amount of flexibility, tensile strength and bending endurance (e.g., plastic bags) the particle size of the inorganic filler will preferably be less than about 10% of the wall thickness of the film. For example, for a blown film having a thickness of 40 microns, it will be preferable for the inorganic filler particles to have a particle size of about 4 microns or less.

On the other hand, thicker-walled articles, particularly those that are intended to be more rigid, may include inorganic fillers having a particle size up to about 50% of the wall thickness. Thus, for a rigid box having a wall thickness of 2 mm, the inorganic filler particles may have a particle size of up to about 1 mm. Due to the tremendous variety of articles and applications that are possible using the thermoplastic starch compositions of the invention, the preferred particle size may vary greatly. As the range of acceptable particle size increases, it may become more desirable to use particle packing techniques in order to incorporate more inorganic filler without comprising mechanical and strength performances. Based on the teachings of this disclosure, one of ordinary skill in the art will be able to optimize the particle size (or range of particle sizes) for a given application.

The amount of particulate filler added to the thermoplastic starch compositions of the invention will depend on a variety of factors, including the quantity and identities of the other added components, as well as the specific surface area and/or packing density of the filler particles themselves. Accordingly, the concentration of particulate filler within the

thermoplastic starch compositions of the present invention may be included in a broad range from as low as about 5% by volume to as high as about 90% by volume of the thermoplastic starch composition. Because of the variations in density of the various inorganic fillers than can be used, it may be more correct in some instances to express the concentration of the inorganic filler in terms of weight percent rather than volume percent. In view of this, the inorganic filler components can be included within a broad range from as low as 5% by weight to as high as 95% by weight of the thermoplastic starch composition.

In those cases where it is desired for the properties of the thermoplastic phase to predominate due to the required performance criteria of the articles being manufactured, the inorganic filler will preferably be included in an amount in a range from about 5% to about 50% by volume of thermoplastic starch composition. On the other hand, where it is desired to create highly inorganically filled systems, the inorganic filler will preferably be included in an amount in a range from about 50% to about 90% by volume.

In light of these competing objectives, the actual preferred quantity of inorganic filler may vary widely. In general terms, however, in order to appreciably decrease the cost of the resulting thermoplastic starch composition, the inorganic filler component will preferably be included in an amount greater than about 15% by weight of the thermoplastic starch composition, more preferably in an amount greater than about 25% by weight, more especially preferably in an amount greater than about 35% by weight, and most preferably in an amount greater than about 50% by weight of the thermoplastic starch composition.

2. Fibers

A wide range of fibers can optionally be used in order to improve the physical properties of the thermoplastic starch compositions of the present invention. Like the aforementioned fillers, fibers will typically constitute a solid phase that is separate and distinct from the thermoplastic phase. However, because of the shape of fibers, i.e., by having an aspect ratio greater than at least about 10:1, they can be added to improve the strength and toughness of the thermoplastic starch compositions. It should be understood, however, that many applications, such as flexible, thin-walled blown bags, may not include any fibers. On the other hand, injection molded and foamed articles will preferably include fibers.

As used in the specification and the appended claims, the terms "fibers" and "fibrous material" include both inorganic fibers and organic fibers. Fibers may be added to the moldable mixture to increase the flexibility, ductility, bendability, cohesion, elongation ability, deflection ability, toughness, and fracture energy, as well as the flexural and tensile strengths of the resulting sheets and articles. Fibrous materials reduce the likelihood that the sheets, films or articles made from thermoplastic starch compositions will shatter when cross-sectional forces are applied.

Fibers that may be incorporated into the thermoplastic starch compositions include naturally occurring organic fibers, such as cellulosic fibers extracted from wood, plant leaves, and plant stems. Virtually any abundant fiber that can be harvested from natural sources will work, although fibers that can be derived from plants that can be harvested in an agribusiness setting can also be utilized in the invention. The use of the second category of fibers would have the additional beneficial effect of preserving our dwindling forests. In addition, inorganic fibers made from glass, graphite, silica, ceramic, rock wool, or metal materials may also be used.

Preferred fibers include cotton, wood fibers (both hardwood or softwood fibers, examples of which include southern hardwood and southern pine), flax, abaca, sisal, ramie, hemp, and bagasse because they readily decompose under normal conditions. However, other fibers such as glass fibers may be preferred depending on the intended use and performance criteria of the sheet or article. Even recycled paper fibers can be used in many cases and are extremely inexpensive and plentiful.

The fibers used in making the sheets and other articles of the present invention preferably have a high length to width ratio (or "aspect ratio") because longer, narrower fibers can impart more strength to the starch-bound matrix without significantly adding bulk and mass to the matrix. The fibers will have an aspect ratio of at least about 10:1, preferably greater than about 25:1, more preferably greater than about 100:1, and most preferably greater than about 250:1.

The fibers may include one or more filaments, fabrics, mesh or mats, and which may be co-extruded, or otherwise blended with or impregnated into, the thermoplastic starch compositions of the present invention.

The amount of fibers added to the thermoplastic starch compositions will vary depending upon the desired properties of the final molded article, with tensile strength, toughness, flexibility, and cost being the principle criteria for determining the amount of fiber to be added in any mix design. Accordingly, the concentration of fibers within the thermoplastic starch compositions of the present invention can be included in a broad range from 0% to about 90% by weight of the thermoplastic starch composition. Preferably, fibers will be included in an amount in a range from about 3% to about 80% by weight of the thermoplastic starch composition, more preferably in a range from about 5% to about 60% by weight, and most preferably in a range from about 10% to about 30% by weight of the thermoplastic starch composition.

It will be appreciated that the strength and other mechanical properties of the fiber will be a very important feature in determining the optimal amount of the fiber to be used. The greater the tensile strength of the fiber, the less fiber that will generally be required to impart a given tensile strength in the resulting product. While some fibers have a high tensile, tear, and burst strength, other types of fibers with a lower tensile strength may be more elastic and flexible. Including higher concentrations of fibers will be particularly useful in these cases where relatively large quantities of inorganic filler have been added such that certain mechanical properties have been compromised. Including a substantial quantity of fibers, which are generally far less expensive than starch/polymer melts, can restore many of the properties that may be diminished as a result of including the inorganic filler component.

In many cases it may be advantageous to include different types of fibers that impart differing properties to the thermoplastic starch compositions. In this way the fibers can even impart synergistic properties to the thermoplastic starch composition. For example, some fibers, such as southern pine and abaca, have high tear and burst strengths, while others, such as cotton, have lower strength but greater flexibility. In the case where both strength and flexibility are desired, a combination of fibers having varying strength and other mechanical properties can be added to the mixture.

Many fibers such as cellulosic fibers have an affinity for water. As such, they can act as a moisture reservoir to help regulate the moisture content of the thermoplastic starch compositions by absorbing or releasing moisture in response to fluctuations in the moisture content of the thermoplastic

starch composition. Nevertheless, if it is desirable to reduce the water affinity of the fibers, better water resistance can be obtained by treating the fibers with rosin and alum ($\text{Al}_2(\text{SO}_4)_3$ or $\text{NaAl}(\text{SO}_4)_2$), which precipitates out the rosin onto the fiber surface, making the surface highly hydrophobic. The aluminum floc that is formed by the alum can create an anionic adsorption site on the fiber surface for a positively charged organic binder such as a cationic starch. Fibers may even be treated with lipids, fatty acids, and salts of fatty acids in order to make them less hydrophilic.

3. Organic Fillers

The thermoplastic starch compositions of the present invention may also include a wide range of organic fillers. Depending on the melting point of the organic filler being added, the filler may remain as a discrete particle and constitute a solid phase separate from the thermoplastic phase, or it may partially or wholly melt and become partially or wholly associated with the thermoplastic phase. One of ordinary skill in the art will be able to determine before hand, or through routine testing, whether a particular organic filler will remain as a discrete particulate filler or become at least partially associated with the thermoplastic phase. Whether it is desired for the organic filler to be a filler or thermoplastic material will depend on the particular application or use of the resulting thermoplastic starch composition.

Organic fillers may comprise a wide variety of natural occurring organic fillers such as, for example, seagel, cork, seeds, gelatins, wood flour, saw dust, milled polymeric materials, agar-based materials, and the like. Organic fillers may also include one or more synthetic polymers of which there is virtually endless variety. Because of the diverse nature of organic fillers, there will not generally be a preferred concentration range for the optional organic filler component.

C. Void Phase

In addition to the foregoing thermoplastic and solid phases, it is within the scope of the invention to incorporate a void phase, generally consisting of a gaseous substance, in order to reduce the mass per unit volume (i.e. density) of the resulting thermoplastic starch composition. Like the inorganic and organic fillers, voids occupy volume that would otherwise be occupied by the thermoplastic phase and tend to therefore reduce the materials costs of the final thermoplastic starch composition. Voids can also increase the insulating ability of articles manufactured from thermoplastic starch compositions. Like other fillers, the inclusion of void spaces can, in some cases, significantly decrease the strength of articles manufactured from the thermoplastic starch compositions. Thus, the amount of voids in relation to the other components should be controlled in order to yield materials having the requisite density and/or insulation properties while maintaining adequate strength for the intended use or application of the thermoplastic starch composition.

There are a variety of ways to introduce voids within the thermoplastic starch compositions of the present invention, including mechanical and chemical means. For example, voids can be introduced into the thermoplastic starch compositions while in a molten state by means of high shear mixing. High shear auger extruders are one example of a high shear mixing apparatus that may be used to incorporate voids within the thermoplastic starch compositions. Because the thermoplastic starch compositions are generally processed at elevated pressures, the void volume will tend to increase as the materials are exposed to atmospheric pressures but will tend to decrease as the materials are cooled.

The relationship between expansion and contraction of the void spaces during processing can be considered when determining how much void space to be incorporated by mixing. Examples of gases that might be entrained within the thermoplastic starch compositions to form a void phase therein include, but are not limited to, air, CO_2 , nitrogen, noble gases, and the like.

Alternatively, or in conjunction with mechanical incorporation of void spaces, it may be advantageous to use volatile solvents or other liquids that can vaporize and thereby yield void spaces as the thermoplastic starch compositions are heated and/or exposed to reduced pressure. Solvents and other liquids which may be considered to be "volatile" within the scope of the present invention include any liquid or solvent that has a vapor pressure that is significantly greater than 1 bar at the melt temperature of the particular thermoplastic starch composition in question. Examples include water, alcohols (such as methyl, ethyl, isopropyl and the like), ketones (such as acetone, methyl ethyl ketone and the like), aldehydes (such as formaldehyde, acetaldehyde and the like), carboxylic acids (such as formic, acetic acid and the like), acid anhydrides (such as acetic anhydride and the like), esters (such as ethyl acetate and the like), amines, and many other well-known solvents and liquids. Solid nucleating agents may be used in conjunction with volatile liquids to assist in forming discrete and well-formed voids. The solid nucleating agents may comprise water-soaked fibers.

Alternatively, or in conjunction with the foregoing void forming methods, it may be preferable in some cases to use chemically reactive foaming agents. An example of a chemically reactive foaming agent is a mixture of citric acid and bicarbonate, or bicarbonate that has been processed into small particles and coated with wax, starch, or water soluble coatings. Upon heating, the bicarbonate will decompose and yield carbon dioxide gas as a reaction product, which acts to expand the thermoplastic starch composition.

There are a wide variety of lightweight fillers that include significant quantities of void spaces. Thus, to the extent that a substantial fraction of the overall volume of a lightweight filler actually comprises voids, then the lightweight filler technically consists of both a solid phase as well as a void phase when viewed microscopically. Examples of lightweight filler that have substantial void space include, but are not limited to, hollow glass spheres, porous ceramic spheres, perlite, vermiculite, exfoliated geologic materials, and the like. Because such lightweight filler tend to be somewhat fragile, it will be preferable to use low shear mixing when blending such fillers within the thermoplastic starch compositions of the present invention.

Another class of void forming agents include filler particles that are able to expand when heated. For example, an expandable particle may include a volatile liquid surrounded by a plastic or otherwise expandable shell. Upon heating, the volatile liquid undergoes a phase change from a liquid to a gas, which causes its volume to expand. This, in turn, causes the surrounding expandable shell to expand to thereby form a lightweight balloon or sphere. One such expandable particle, available from Akzo-Nobel located in Sweden, comprises an acrylonitrile shell surrounding a core of hexanes or heptanes which, upon heating, forms a lightweight balloon or sphere.

D. Effect of Components on Thermoplastic Starch Compositions While in a Molten State

In general, the viscosity and other Theological properties of the thermoplastic starch compositions of the invention while in a molten state will directly relate to the type and

amounts of the various components within the composition. Of course, while the thermoplastic starch composition might be "molten" when viewed macroscopically, the thermoplastic starch compositions will generally include both molten and solid components. Typically, the thermoplastic starch compositions while in a melted or molten state will include a generally liquid or plastic thermoplastic phase in a melted or molten state that comprises a continuous phase or matrix and one or more generally solid disperse phases comprising inorganic filler particles and optionally fibers, organic fillers, and other solid components. A void phase comprising gas-filled voids may also be optionally included.

The viscosity of the molten thermoplastic phase itself will be dependent on the viscosity of the thermoplastic starch melt, optional thermoplastic polymers, and other liquid components within the thermoplastic phase while in a molten state. Although the viscosity of the thermoplastic starch melt portion will depend to some degree on the type of plasticizer and starch being used (e.g., the source, such as potato or corn, or the degree to which is has been modified or denatured), the viscosity will especially depend on the amount of plasticizer that is added in relation to the starch content. As more plasticizer is added, the viscosity of the starch melt will typically decrease at a given temperature. In general, adding liquids and additional thermoplastic polymers having viscosities that are lower or greater than that of the starch melt will tend to lower or raise the viscosity of the molten thermoplastic phase, respectively.

In addition, any reactions between the starch, polymer and other components might affect the viscosity of the thermoplastic melt phase. As a general rule, but by no means the absolute rule in every case, reactions that result in polymer molecules having increased molecular weight will tend to increase the viscosity of the thermoplastic melt phase. Thus, cross-linking reactions between the starch molecules themselves or between other components within the thermoplastic starch composition will tend to increase the viscosity of the mixture. Similarly, reactions between the starch molecules and, e.g., the optional synthetic polymers, such as by addition, etherification, esterification, and the like will tend to increase mixture viscosity. On the other hand, hydrolysis or other cleaving reactions will tend to decrease mixture viscosity, all other things being equal.

Because the inorganic filler and optional fibrous components will remain as discrete solids in most cases, and will not undergo a state change or become part of the thermoplastic phase, they will tend to increase mixture viscosity, particularly at higher concentrations. Thus, increasing the concentration of inorganic filler and optional fibrous components will tend to increase the viscosity of the thermoplastic starch compositions. Other factors that will affect mixture rheology include the morphology and specific surface area of the inorganic filler particles and optional fibers. In general, increasing the specific surface area and/or the irregularity of the filler particles and fibers will increase the viscosity since more of the thermoplastic phase will be required to coat and lubricate the inorganic filler particles and fibers. Conversely, decreasing the specific surface area and/or irregularity of the particle and fiber surfaces will decrease the viscosity, all other things being equal.

In addition, increasing the particle packing density of the inorganic filler particles can greatly reduce the viscosity of the molten thermoplastic starch compositions. By way of example, an inorganic filler particle system having a packing density of 0.65 will generally require about 35% by volume of the thermoplastic phase to substantially fill the interstitial space between the particles. On the other hand, a filler

particle system having a packing density of 0.95 will generally require only about 5% by volume of the thermoplastic phase to substantially fill the voids. At the point where there is just enough of the thermoplastic phase to fill the void spaces between the filler particles, even slight fluctuations in the concentration of the thermoplastic phase can greatly affect the mixture rheology. In the example herein, a filler having a particle packing density of 0.65 will require seven times the amount of thermoplastic phase as a filler having a particle packing density of 0.95 to roughly achieve the same level of particle lubrication. This clearly shows the potentially substantial effects of particle packing density on mixture rheology.

The inclusion of other admixtures such as dispersants, plasticizers and lubricants can greatly affect mixture rheology. Dispersants such as sulfonyl-based materials greatly decrease the viscosity and increase the workability of the moldable mixture while keeping the amount of thermoplastic phase constant. In addition, water scavengers such as zeolites and hydraulically reactive materials can affect mixture rheology by eliminating water that might otherwise act to lubricate the thermoplastic starch composition and/or that might inhibit condensation reactions between the starch and other polymers within the thermoplastic phase.

Organic fillers can affect mixture rheology in a variety of ways depending on the chemical makeup and physical properties of the organic filler being used. In the case where the organic fillers have a melting point above the softening point or range of the thermoplastic phase such that they will remain essentially as solid particulate material, their effect on mixture rheology will be similar to that of the inorganic filler particles. However, to the extent that the organic filler particles melt or at least soften due to increases in temperature, their viscosity-increasing effect will be lessened. On the other hand, to the extent that the organic filler chemically reacts with the starch and/or other polymer component, the organic filler might tend to further increase the viscosity of the molten thermoplastic starch composition.

Of course, the biggest changes in mixture rheology will occur as a result of state changes of the thermoplastic phase between solid and liquid states due to fluctuations in temperature, particularly in the region of the melting point or softening range of the thermoplastic starch composition.

E. Effect of Components on Properties of Thermoplastic Starch Compositions When Solidified

With regard to the final thermoplastic starch composition, important mechanical, chemical, and other properties include tensile strength (in general or along particular vectors), compressive strength, flexibility, modulus of elasticity, ductility, fracture energy, the ability to elongate, deflect or bend, bending endurance, density, permeability to gases and liquids, resistance to water and other liquids, resistance to water vapor and other gases, thermal resistance, and specific heat.

The foregoing properties can be tailored to the particular performance criteria of the final article by altering the identity and relative concentration of the various components within the thermoplastic starch composition. In some cases, higher tensile strength may be an important feature. In others, it may be less significant. Some articles should preferably be more flexible, while others should be more rigid. Some should be relatively dense, while others should be thicker, lighter, and more insulative. The important thing is to achieve a material which has properties appropriate for a particular use, while remaining cognizant of cost and other practical manufacturing parameters. While having "too

much" or "too little" of a particular property may be inconsequential from the standpoint of performance, from a cost standpoint it may be wasteful, inefficient or ineffectual to provide too much of a particular property, even if desired up to a certain point.

In general, the overall mechanical properties of a particular thermoplastic starch composition will correlate to the properties of the solidified thermoplastic phase. All things being equal, a thermoplastic phase having superior mechanical properties compared to a different thermoplastic phase will yield a thermoplastic starch composition having superior mechanical properties. Due to the tremendous variety of different thermoplastic starch compositions and starch/polymer blends that may be used in the thermoplastic starch compositions within the scope of the present invention, one of ordinary skill in the art will have an almost limitless supply of possible thermoplastic phases and attendant properties from which to choose. In selecting the optimal thermoplastic phase, one of ordinary skill in art will have to understand the performance criteria of the final articles to be manufactured, the cost parameters, and identities, concentrations and associated properties of the other components within the thermoplastic starch composition. In general, it will be preferred to select a thermoplastic phase that has the lowest cost while having adequate, though not necessarily superior, mechanical, chemical and other properties, compared to other possible thermoplastic phases.

In general, increasing the concentration of polymers that have increasing tensile and other strength properties will increase the strength of the resulting thermoplastic starch composition. The degree of water resistance of the thermoplastic phase will, of course, greatly affect the water resistance of the overall composition. The elasticity and toughness of the thermoplastic phase will have a significant effect on the final composition. Increasing the concentration of plasticizer will typically increase the flexibility and elasticity of the thermoplastic phase. Conversely, decreasing the amount of plasticizer will yield a stiffer, more brittle thermoplastic phase. Thus, the identity and concentration of the plasticizer can greatly affect the final properties of the thermoplastic starch composition. Low volatile plasticizers will tend to yield properties that remain substantially constant over time, while more volatile solvents such as water can evaporate away over time, yielding a thermoplastic starch composition whose mechanical properties may change substantially over time.

The degree of crystallinity of the thermoplastic phase can greatly affect the mechanical properties of the thermoplastic starch composition. In general, the more amorphous the thermoplastic phase, the greater will be the tensile strength, flexibility, ductility, bending endurance, and other like properties of the composition. Conversely, the greater the crystallinity of the thermoplastic phase, the greater will be the stiffness, Young's modulus, rigidity, and other like properties of the composition. In general, increasing the concentration of plasticizer will decrease the crystallinity of the thermoplastic phase, thereby making it more amorphous. In addition, the addition of dissimilar materials, such as additional polymers, blocking agents, and the like within the starch melt will tend to result in a solidified thermoplastic phase that is more amorphous and less crystalline in nature.

All things being equal, for a given thermoplastic phase, increasing the concentration of the inorganic filler component will tend to decrease the tensile strength, reduce the flexibility, increase the stiffness, increase the compressive strength, decrease the ductility, and decrease the fracture energy of the resulting thermoplastic starch composition.

The effect of the inorganic filler on the density will usually depend on the relationship between the density of the filler and the thermoplastic phase. Because most of the less expensive inorganic fillers have a density that is typically greater than most thermoplastic phases, increasing the inorganic filler content will generally increase the density of the thermoplastic starch composition. However, certain lightweight fillers can actually lower the density of the thermoplastic starch composition. Lightweight fillers will also generally lower the thermal conductivity and specific heat of the thermoplastic starch composition, while the effect of other inorganic fillers on such properties is variable.

Because the general effect on desirable strength and other mechanical properties by adding the inorganic filler can be negative, such negative effects can be offset by adding reinforcing fibers. Of course, fibers may also be added to impart these and other properties independent of the inorganic filler. In general, including more fibers will tend to increase the tensile strength, flexibility, compressive strength, tear and burst strength, ductility, fracture energy, and modulus of elasticity of the resulting thermoplastic starch composition. In general, using longer, more flexible fibers will generally impart more flexibility to the thermoplastic starch composition compared to shorter, stiffer fibers. In order to obtain the advantageous properties of different types of fibers, it may be preferable in some cases to combine two or more different kinds of fibers within the thermoplastic starch composition. It should also be understood that shaping processes, such as extrusion and rolling, will tend to orient the fibers in the direction of elongation of the thermoplastic starch composition. This may be advantageous in order to maximize, e.g., the tensile strength, flexibility, and bending endurance of the resulting article in a certain direction.

Finally, other admixtures within the thermoplastic starch composition such as cross-linking agents, lubricants, humectants, plasticizers, hydroxyl blocking groups, and the like can greatly affect the final properties, such as resistance to water or other liquids, impermeability to water vapor or other gases, ductility and strength.

The thermoplastic starch compositions formed using the compositions described herein will preferably have a tensile strength in the range from about 0.1 MPa to about 500 MPa, and more preferably in the range from about 5 MPa to about 200 MPa.

III. Manufacturing Thermoplastic Starch

Compositions and Articles Therefrom

A. Formation of Molten Thermoplastic Starch Compositions

In order to manufacture thermoplastic starch compositions according to the present invention, it is first necessary to create a thermoplastic melt of the thermoplastic starch composition. A preferred method for manufacturing thermoplastic starch compositions according to the present invention includes: (1) causing the starch component to behave in a thermoplastic manner to form in an initial thermoplastic phase; (2) optionally blending one or more additional polymers and/or other materials with the starch melt to form multicomponent thermoplastic phase; (3) mixing the solid phases including the inorganic filler phase, optional fibrous phase, and other optional solid phases into the thermoplastic phase; (4) optionally forming a void phase; (5) shaping the thermoplastic starch composition while in a melt state; and (6) allowing the molten starch composition to cool below the softening point or range and thereby form a solid article of manufacture. The foregoing sequence is illustrative but not limiting, and the components may be blended together in any order so long as the resulting thermoplastic starch

composition has the desired characteristics. Moreover, the composition may be solidified into beads and then remelted prior to final shaping into the desired article.

1. Creating a Starch Melt

In order to form a starch melt, it is necessary to heat native ungelatinized starch granules in the presence of a plasticizer, preferably in the presence of significant shearing forces to thoroughly blend the plasticizer and starch granules together during the melt procedure. As set forth above, a wide variety of different starches and starch derivatives may be used within the thermoplastic starch compositions of the present invention. Moreover, a wide variety of plasticizers can be used to lower the melting point of starch so that it can form a melt instead of decomposing, which will occur if one were to attempt to form a starch melt by heating in the absence of a plasticizer.

The type of plasticizer that is used can greatly affect the properties of the resulting thermoplastic starch melt. Moreover, using predried starch in which a substantial portion of water naturally found in the starch granules has been removed prior to formation of the starch melt can have a beneficial effect, particularly where it is desired for the starch to undergo a condensation reaction with another thermoplastic polymer or other material in the thermoplastic starch composition. A detailed description of preferred methods for forming a starch melt using either native or pre-dried starch is set forth in U.S. Pat. No. 5,362,777 to Tomka. In the case of native starch, water is removed during the process of mixing the starch and plasticizing additive together according to Tomka. A number of other patents teach useful methods for forming thermoplastic starch melts using an initial quantity of water and one or more less volatile plasticizers, wherein water is removed during processing while in a melt phase by degassing, including U.S. Pat. No. 5,412,005 to Bastioli et al. Finally, U.S. Pat. No. 5,095,054 to Lay et al. discloses processes for forming a destructure starch melt using water as the primary melting aid. Although the foregoing patents disclose varying plasticizers and thermoplastic polymers that may be blended with the starch melts, each of the patents discloses useful process conditions for forming a starch melt. For purposes of disclosing a range of processes for forming a starch melt, the patents identified in this paragraph are incorporated herein by specific reference.

Depending on the identities and concentrations of both the starch and plasticizer components, it is possible to create a molten starch material within a wide range of temperatures. As a general rule, increasing the ratio of plasticizer to starch will tend to decrease the temperature at which the starch/plasticizer mixture will become molten. Conversely, increasing the starch to plasticizer ratio will tend to increase the temperature at which starch can be melted. Selecting the optimal ratio of starch and plasticizer will depend on a number of factors, including the desired melt temperature, desired rheology of the molten starch melt, and the desired final properties of the thermoplastic starch composition. Including more of the plasticizer initially, particularly if it cannot later be removed by, e.g., evaporation, will further tend to yield a softer, more flexible thermoplastic starch composition. When selecting the amount of plasticizer to add, enough plasticizer should be added in order to prevent the melting point or softening range from being so high as to risk excessive decomposition of the starch during the melt process. On the other hand, the melting point or softening range of the resulting starch melt should not be so low so as to yield a thermoplastic starch composition that will become inappropriately soft or molten during the useful life of

articles manufactured therefrom. In general, the intended use for the article to be manufactured from the thermoplastic starch composition can help determine the lower limit of melt temperatures that would be appropriate. The intended use may also help determine the targeted glass transition temperature or range, which can be adjusted, for example, by selecting an appropriate polymer to be added to the thermoplastic starch composition having a glass transition temperature within a desired range.

In view of the foregoing, the starch/plasticizer mixtures within the scope of the present invention will preferably form a melt at a temperature (or range of temperatures) in a range from about 70° to about 240° C., more preferably in a range from about 80° C. to about 220° C., and most preferably from a range from about 100° C. to about 200° C.

In the case where a substantial amount of water is used as a plasticizing agent, it will typically be necessary to maintain the starch melt within a closed vessel in order to prevent evaporation of the water and premature solidification of the starch melt. Nevertheless, it may be preferable in many cases to vent some or all of the water, particularly where a low volatile plasticizer is used, in order to reduce or eliminate the water altogether. In the case where a sufficient quantity of a low volatile plasticizer is used, it may not be essential for the starch melt to remain within a closed vessel. Thus, virtually any mixing apparatus capable of imparting the requisite shear can be used within the scope of the invention. These include Hobart mixers, high energy cement mixers, potato mixers, and the like. Nevertheless, a preferred mixing apparatus will comprise the interior of single and multiple auger extruders.

Preferable auger extruders include multiple ports for introducing various ingredients, multiple chambers for mixing the various ingredients at different stages of the mixing process, one or more heating zones in order to raise the temperature of the thermoplastic starch melts to one or more temperatures, and an optional degassing chamber that can be used to release unwanted volatiles, such as water vapor. There are a wide variety of extruders that may be used, including most extruders used in the plastics and ceramic industries, with or without modification. One of ordinary skill in the art will be able to select and optionally modify any known extruder used in the art to provide adequate processing conditions. A preferred apparatus for manufacturing starch melts and compositions therefrom may be found in U.S. Pat. No. 5,525,281 to Lörcks, et al. For purposes of disclosing suitable mixing and processing apparatus for forming thermoplastic starch compositions within the scope of the present invention, the foregoing patent is incorporated herein by specific reference.

Suitable mixing apparatus that can be used to form starch melts include: a twin-shafted kneader with meshing screws having kneading blocks sold by the Buss Company; a Brabender mixer; a Theysohn TSK 045 compounder, which is a twin-shaft extruder with shafts rotating in the same direction and which has multiple heating and processing zones; a Buss Ko-Kneader having a heatable auger screw; Baker-Perkins MPC/V-30 double and single auger extruder; single and twin auger OMC extruders; Model EPV 60/36D extruder; BATTAGGION ME100 direct-current slow mixer; and a HAAKE Reomex extruder.

2. Blending Additional Polymers and Liquids to Form the Thermoplastic Phase

As set forth above, one or more natural or synthetic polymers may be added to the starch melt in order to improve the properties of the thermoplastic starch compositions, particularly in the solid state. In addition,

other materials such as liquids, solids, and gases can be dissolved or otherwise incorporated into the thermoplastic phase in order to further improve the properties thereof. Such other polymers and materials will preferably be added to the starch after the starch has at least partially formed a melt in order that the starch and optional polymers and other materials can then be substantially homogeneously mixed together. Typically, the thermoplastic phase will be subjected to high shear conditions within an appropriate mixer. Where it is desired for the process to be continuous, the same apparatus used to form the starch melt may be used to blend the other components therein. More preferably, the mixing apparatus will comprise an auger extruder as discussed above. Multi-chamber extruders advantageously allow for the addition of different materials downstream from where previous materials have been added, melted and blended in order to form a continuous and dynamic mixing process that takes advantage of the proper order of mixing selected components together.

In many cases it will be advantageous for the starch and one or more synthetic polymers to undergo a condensation reaction (or other type of reaction) in order to chemically interlink at least a portion of the starch with at least a portion of one or more additional polymers. Such chemical linking yields a more homogeneously mixed thermoplastic phase having more uniform properties. In addition, reacting the starch and other polymer(s) creates greater strength by virtue of the formation of a larger number of chemical bonds throughout the thermoplastic phase. Additional cross-linking agents, chain extenders and reactants may also be added in order to further improve the properties of the thermoplastic phase.

In order to assist in the promotion of condensation reactions between the starch and other components, it will be preferable to minimize the amount of water within the thermoplastic phase melt. As set forth above, a preferred method of doing this is to use starch that has been pre-dried to remove a substantial portion of the water inherently bound within native starch, which is typically about 10-20%. Preferred pre-dried starch will have a water content less than about 10%, more preferably less than about 5%, and most preferably less than about 3% by weight of the starch.

In order to further reduce the moisture content beyond that which may be removed by way of pre-drying the starch, the mixing apparatus may be equipped with a venting chamber or other degassing means for further venting or degassing water in a vapor form during processing. Since the thermoplastic phase will typically melt at a temperature higher than the boiling point of water, water vapor can be advantageously removed by means of venting. Moreover, because there is some reason to believe that starch thermodynamically prefers associating with glycerin, sorbitol and other plasticizing liquids compared to water, it may be easier to remove water during processing compared to pre-drying the starch, particularly without damaging the starch. In addition, venting or degassing can be employed to remove any moisture that may be produced by way of condensation reactions between starch and other components during the formation of the thermoplastic starch composition.

In the case where condensation reactions are dynamically occurring throughout the thermoplastic melt phase, it is possible that farther water may be produced as a by product. Removal of this water of condensation and any residual water within the pre-dried starch can assist in driving the desired condensation reaction in the forward direction in order to more fully react the starch and the synthetic thermoplastic components.

In the case where water is removed by degassing or venting of the thermoplastic starch composition during processing, it will be preferable to remove water so that the composition includes less than about 5% water by weight of the combined starch, plasticizer and water content while in a melted state, more preferably less than about 3% by weight, and most preferably less than about 1% by weight while in a melted state. As will be discussed below, upon cooling the melt, such as by means of water, the quenched melt will tend to reabsorb moisture. However, moisture that is reabsorbed is loosely bound in the sense that it is believed not to become interposed between the starch molecules as are the water or other plasticizer that is mixed with the starch while in a molten state. As such, this loosely bound water does not participate in the thermoplastic starch on a molecular level in the same way that "integrated" water or plasticizer is involved, and the transient nature of such moisture and its tendency to migrate into or out of the thermoplastic starch composition does not yield retrograde or crystalline starch as does the migration of "integrated water" out of deconstructured starch.

Because it is certainly within the scope of the present invention to utilize thermoplastic polymers that do not undergo condensation reactions with the starch component, or that do not react at all with the starch, it will not be necessary in every case to use pre-dried starch and/or vent water from the thermoplastic phase melt. Of course, to the extent that water vapor might damage the mechanical integrity of the thermoplastic starch compositions upon exiting from the extruder barrel, it will certainly be preferable to remove any deleterious amounts of water vapor.

In most cases, it will be preferable to blend the starch and one or more additional polymers with sufficient shear and for a sufficient length of time to yield a substantially homogeneous mixture. Because the starch molecules and other thermoplastic polymer molecules are relatively large in size, the resulting thermoplastic phase will typically comprise multiple subphases of two or more different types of polymers. As a general rule, the more cross linking bonds there are between the various polymer molecules of the different subphases the greater will be the strength and uniformity of mechanical properties of the thermoplastic starch composition.

In those cases where the melting point or softening range of the thermoplastic starch melt is higher than the melting point or softening range of the optionally added polymers, it will usually not be necessary to further increase the temperature of the thermoplastic phase in order to cause the other polymers to melt. On the other hand, in those cases where the temperature of the starch melt is significantly lower than the melting point or softening range of the one or more added polymers, it may be necessary to increase the temperature that is applied to the thermoplastic melt in order to obtain a homogeneously blended melt. Nevertheless, it is certainly within the scope of the present invention to only partially melt one or more components of the thermoplastic phase if desired. Moreover, it may be possible in some cases for a polymer blend to have an overall melting point or softening range that is lower than the melting point or softening range of the individual polymers.

3. Addition of Solid Phases

A wide variety of solid phases such as one or more inorganic fillers and optional fibrous and organic fillers can be added to the thermoplastic starch compositions. In the event that fibers are added, it will generally be preferable to add the fibers to the thermoplastic phase melt prior to the addition of the inorganic filler, since fibers generally require

greater shearing action than inorganic fillers to become homogeneously mixed. The thermoplastic phase will preferably have a viscosity that is sufficient to transfer the shearing action of the mixing apparatus down to the fiber level in order to separate the fibers and homogeneously disperse them throughout the thermoplastic phase.

Because the inorganic filler components will generally comprise particulate fillers that are generally easier than fibers to disperse throughout the thermoplastic phase, blending such fillers will require much less shear compared to the blending of the fibrous materials. Moreover, because the inorganic filler component will generally be far more abrasive than the other components that may be added to the composition, it may be advantageous to use less shear in order to protect the components of the mixing apparatus. Nevertheless, any degree of shear can be used so long as it yields a thermoplastic composition and does not unduly damage the mixing apparatus.

In those cases where fragile inorganic fillers are included, such as lightweight fillers that include significant void spaces, excessively high shearing forces can cause such fillers to break and be ground into a finer powder, which would thereby destroy the lightweight and/or insulating effect of such materials.

Organic filler components may generally be added at any time either before or after the addition of the inorganic filler. It should be understood, however, that certain specific components may be best blended in specific orders and sequences under certain optimal mixing conditions. One of ordinary skill in the art will know how to optimize the mixing order and mixing conditions in order to obtain thermoplastic starch compositions having desired properties, both in the melt state and in the solid state.

4. Forming Optional Void Phase

In those instances where it may be desired to incorporate a void phase, a wide variety of different techniques may be used to introduce voids, such as the use of mechanical means, blowing agents, nucleating agents, chemical expansion agents, expandable particles, and the like. Void forming agents may be added at any time during the manufacture of the thermoplastic phase, either before, during or after the addition of the solid phases. In general, it will be advantageous for the blowing agent to have its maximum expansion effect during the molding process in which the final articles are formed. Nevertheless, voids may be introduced during the mixing process, molding process, or during a post molding process in which a final article is heated to a temperature sufficient to cause the thermoplastic phase to become at least partially molten while simultaneously triggering some kind of expansion agent to form void spaces within the molded article.

B. Shaping of Molten Thermoplastic Starch Compositions

Once the thermoplastic starch compositions have been processed into a molten state, they may be shaped into a huge variety of articles using any known shaping means known in the art for plastic materials. Moreover, many shaping procedures used to form other materials such as ceramics may be modified and used to mold the thermoplastic starch compositions, particularly those that include a relatively high concentration of inorganic filler.

In many cases it will be desirable to first form the thermoplastic starch compositions into a granulate or bead by extruding the initially formed thermoplastic starch compositions through a die to form an extruded strand, which is thereafter cooled in a water bath, and then chopped into individual pieces. Such pieces may be stored, transferred and then used as desired in the manufacture of a wide variety

of articles. Alternatively, the molten thermoplastic starch compositions can be immediately molded into the desired final articles.

Cooling an extruded strand with water prior to formation of a granulate will tend to cause a net absorption of water in the granulate. The absorption of water begins at the moment the extrudate is cooled or quenched in water, and continues so long as the strand or granulates are moist and/or exposed to relatively humid ambient conditions. Of course, water that is reabsorbed should be understood to be "loosely bound" in the sense that once the thermoplastic starch phase has solidified, the absorbed water is only absorbed superficially and is not believed to become incorporated substantially within and between the starch molecules in the same manner as the water and/or plasticizer that is mixed with the starch while in a melted state. In general, thermoplastic starch compositions that are cooled with water will absorb from about 1% to about 6% by weight of loosely bound water.

Appropriate molding processes used to form the thermoplastic starch compositions of the invention into desired articles include blow molding, film blowing, injection molding, die press molding, rolling or calendering to form sheets, vacuum forming, including vacuum forming of sheets and films, extrusion, hot pressing, laminating, coating, and virtually any other known molding technique. A preferred blow-molding apparatus is an AEMME-200 blow-molding apparatus.

In most cases, the shaping process also includes cooling the shaped thermoplastic starch composition to below its melting point or softening range in order to yield a solidified article. Depending on the type of article being manufactured, as well as the intended use of the article, it may be preferable to control the degree of crystallinity of the solidified thermoplastic phase. In most cases, the type and quantity of plasticizer and other polymers blended with the starch component will have the greatest effect on the crystallinity of the thermoplastic phase, as discussed more fully above. Nevertheless, it may also be possible to affect the degree or percentage of crystallinity by controlling the rate at which the shaped thermoplastic starch compositions are cooled.

As with other polymers, the degree of crystallinity of the starch molecules and other polymers within the thermoplastic phase may be increased if the molten thermoplastic starch compositions of the present invention are cooled more slowly. For example, if a starch melt is cooled slowly so that its temperature is maintained within the softening range for a relatively long time, the molecules may be allowed to rearrange themselves into a lower energy crystalline state. On the other hand, cooling a starch melt more quickly will tend to maintain the solidified product in a more amorphous, and less crystalline state.

Controlling the degree of crystallinity by means of controlling compositional as well as processing variables, may be helpful in engineering a final product having desired properties. On the one hand, solidified thermoplastic starch compositions that have lower crystallinity and which are more amorphous will generally have greater tensile strength, flexibility, bending endurance, and will behave like a wide variety of conventional thermoplastic polymers. On the other hand, such compositions will generally be more sensitive to heat over a wider range of temperatures. Thus, more highly crystalline thermoplastic compositions may be more suited for the manufacture of articles that need to be more heat-resistant, such as microwavable containers. Because more amorphous compositions tend to soften at lower temperatures due to such polymers having a wider softening range compared to crystalline polymers which have a more

distinct melting point, they may have the tendency to soften when heated in a microwave oven. In contrast, compositions having a greater degree of crystallinity will tend to remain more rigid until heated to even higher temperatures and for longer periods of time compared to more amorphous polymers. The same is true for more amorphous polymers that are cooled to or below their glass transition temperature.

As stated above, preferred melting points or softening ranges for the thermoplastic starch compositions of the present invention are in a range from about 70° C., to about 240° C., more preferably in a range from about 80° C. to about 220° C., and most preferably in a range from about 100° C. to about 200° C.

C. Post-Formation Processing

Once an appropriate article has been formed from the inventive thermoplastic starch compositions, it may be further processed in order to obtain the desired mechanical or physical properties. Post-formation processes include conversion of one article into another, such as the formation of containers or other articles from sheets, remelting, coating, monoaxial and biaxial stretching of sheets, lamination with one or more other sheets or films, corrugation, creping, parchenting, scoring and perforation of sheets, printing, expansion, and virtually any other known post-formation process.

Coatings that may be used with the thermoplastic starch compositions of the present invention include paraffin (synthetic wax); shellac; xylene-formaldehyde resins condensed with 4,4'-isopropylidenediphenolepichlorohydrin epoxy resins; polyurethanes; drying oils; reconstituted oils from triglycerides or fatty acids from the drying oils to form esters with various glycols (butylene glycol, ethylene glycol), sorbitol, and trimethylol ethane or propane; synthetic drying oils including polybutadiene resin; natural fossil resins including copal (tropical tree resins, fossil and modern), damar, elemi, gilsonite (a black, shiny asphaltite, soluble in turpentine), glycol ester of damar, copal, elemi, and sandarac (a brittle, faintly aromatic translucent resin derived from the sandarac pine of Africa), shellac, Utah coal resin; rosins and rosin derivatives including rosin (gum rosin, tall oil rosin, and wood rosin), rosin esters formed by reaction with specific glycols or alcohols, rosin esters formed by reaction formaldehydes, and rosin salts (calcium resinate and zinc resinate); edible oils; phenolic resins formed by reaction of phenols with formaldehyde; polyester resins; epoxy resins, catalysts, and adjuncts; coumarone-indene resin; petroleum hydrocarbon resin (cyclopentadiene type); terpene resins; urea-formaldehyde resins and their curing catalyst; triazine-formaldehyde resins and their curing catalyst; modifiers (for oils and alkyds, including polyesters); vinyl resinous substances (polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, etc.); cellulosic materials (carboxymethylcellulose, cellulose acetate, ethylhydroxyethylcellulose, etc.); styrene polymers; polyethylene and its copolymers; acrylics and their copolymers; methyl methacrylate; ethyl methacrylate; waxes (paraffin type I, paraffin type II, polyethylene, sperm oil, bees, and spermaceti); melamine; polyamides; polylactic acid, Biopol® (a polyhydroxybutyrate-hydroxyvalerate copolymer), polycaprolactone and other aliphatic polyesters; aliphatic-aromatic copolyesters; soybean protein; latexes; polyacrylates; other synthetic polymers including biodegradable polymers; and elastomers and mixtures thereof. Appropriate inorganic coatings include sodium silicate, calcium carbonate, aluminum oxide, silicon oxide, kaolin, clay, ceramic and mixtures thereof. The inorganic coatings may also be mixed with one or more of the organic coatings set forth above.

Of course, it should be understood that the thermoplastic starch compositions of the present invention may themselves be used as coating materials in order to form a synergistic composite with, or otherwise improve the properties of, any number of other materials. Such disparate materials such as paper, paperboard, molded starch-bound articles such as starch-based foams, metals, plastics, concrete, plaster, ceramics, and the like can be advantageously coated with a thermoplastic starch composition.

D. Articles Made From Thermoplastic Starch Compositions

Due to the wide variety of properties that may be microstructurally engineered into the thermoplastic starch compositions of the present invention, it is possible to manufacture a wide variety of finished articles that may presently be made plastics, paper, paperboard, polystyrene, metals, ceramics, and other materials. Merely by way of example, it is possible to manufacture the following exemplary articles: films, bags, containers, including disposable and nondisposable food or beverage containers, cereal boxes, sandwich containers, "clam shell" containers (including, but not limited to, hinged containers used with fast-food sandwiches such as hamburgers), drinking straws, plastic baggies, golf tees, buttons, pens, pencils, rulers, cassette tape boxes, CD containers, cassette tapes, business cards, toys, tools, Halloween masks, building products, frozen food boxes, milk cartons, fruit juice containers, yoghurt containers, beverage carriers (including, but not limited to, wraparound basket-style carriers, and "six pack" ring-style carriers), ice cream cartons, cups, french fry containers, fast food carryout boxes, packaging materials such as wrapping paper, spacing material, flexible packaging such as bags for snack foods, bags with an open end such as grocery bags, bags within cartons such as a dry cereal box, multiwall bags, sacks, wraparound casing, support cards for products which are displayed with a cover (particularly plastic covers disposed over food products such as lunch meats, office products, cosmetics, hardware items, and toys), computer chip boards, support trays for supporting products (such as cookies and candy bars), cans, tape, and wraps (including, but not limited to, freezer wraps, tire wraps, butcher wraps, meat wraps, and sausage wraps); a variety of cartons and boxes such as corrugated boxes, cigar boxes, confectionery boxes, and boxes for cosmetics; convoluted or spiral wound containers for various products (such as frozen juice concentrate, oatmeal, potato chips, ice cream, salt, detergent, and motor oil), mailing tubes, sheet tubes for rolling materials (such as wrapping paper, cloth materials, paper towels and toilet paper), and sleeves; printed materials and office supplies such as books, magazines, brochures, envelopes, gummed tape, postcards, three-ring binders, book covers, folders, and pencils; various eating utensils and storage containers such as dishes, lids, straws, cutlery, knives, forks, spoons, bottles, jars, cases, crates, trays, baking trays, bowls, microwaveable dinner trays, "TV" dinner trays, egg cartons, meat packaging platters, disposable plates, vending plates, pie plates, and breakfast plates, emergency emesis receptacles (i.e., "barf bags"), substantially spherical objects, toys, medicine vials, ampules, animal cages, firework shells, model rocket engine shells, model rockets, coatings, laminates, and an endless variety of other objects.

IV. EXAMPLES OF THE PREFERRED EMBODIMENTS

The following examples are presented in order to more specifically teach compositions and process conditions for forming the thermoplastic starch compositions according to the present invention, as well as articles therefrom. The

examples include various mix designs, as well as various processes for manufacturing thermoplastic starch compositions, including sheets, films, pellets, containers, and other articles of manufacture.

U.S. Pat. No. 5,736,209 to Andersen et al., discloses compositions and methods for manufacturing a wide variety of sheets that include starch as the primary binder, a cellulosic ether as a secondary film-forming binder, inorganic fillers up to 90% by weight, and fibers. Such sheets are manufactured from aqueous starch-based mixtures that generally include sufficiently large quantities of water such that the resulting aqueous starch-based mixture will not behave as a thermoplastic material—such starch-based mixtures being liquid or gel-like at room temperature. Therefore, the sheets made from these starch-based mixtures are typically made by passing the mixture between one or more sets of heated sheet-forming rollers which remove a substantial portion of the water by evaporation in order to cause the starch and cellulosic ether binders to resolidify and thereby form a solid sheet.

More recently the inventors discovered that sheets made according to U.S. Pat. No. 5,736,209, when made to include glycerin and/or sufficient residual moisture, could be subsequently reheated and reshaped and, thus, caused to behave in a thermoplastic manner. It was observed that such sheets could be heated to the point that they become softened and somewhat plastic or flowable, which allowed the sheets to be reshaped and then resolidified in the new shape by cooling. Because many of such sheets included significant to substantial quantities of an inorganic filler (e.g., calcium carbonate), it was thereby discovered that compositions that included starch, glycerin and/or water in plasticizing quantities, a cellulosic ether as an auxiliary polymer, calcium carbonate as an inorganic filler, and fibers as reinforcement could be processed in a thermoplastic manner.

Incorporated Example Set I

The following examples from U.S. Pat. No. 5,736,209 are expressly incorporated herein by specific reference as examples of starch-containing compositions that have been found to exhibit thermoplastic behavior: Examples 5, 10, 11, 28, 29, 33–35 and 46–48. Although the sheets were manufactured from aqueous starch-based mixtures that themselves do not behave in a thermoplastic manner, the resulting sheets made by evaporating a substantial portion of the water from the initial aqueous mixtures did, in fact, exhibit thermoplastic behavior when subsequently reheated so as to form a melt. In view of the foregoing, the final sheets and their associated compositions of Examples 5, 10, 11, 28, 29, 33–35 and 46–48 of U.S. Pat. No. 5,736,209, provide actual working examples of compositions that, when subsequently reheated to form a melt, yield thermoplastic starch compositions within the scope of the present invention. The reason why the starch was able to behave in a thermoplastic manner was believed to be due to the inclusion of glycerin within the mixtures disclosed in these examples. The glycerin in the final hardened sheets, either alone or in combination with residual water, acted as a plasticizer that lowered the melt temperature of the starch to below the decomposition temperature of the starch, thus causing the starch to become thermoplastic.

More particularly, starch-bound sheets made generally according U.S. Pat. No. 5,736,209 were passed between a pair of rollers which were configured to exert a pressure of about 60 bars and which were heated to 180° C. The starch-bound sheets were initially generally opaque, which

is characteristic of more highly crystalline retrograde starch formed by removing water by evaporation from gelatinized starch. However, upon being passed between the rollers, the sheet became transparent, which is more characteristic of starch that has undergone a melt so as to become more highly amorphous and less crystalline. In addition, the starch-bound sheet turned from a solid state to a molten thermoplastic starch material, which tended to deposit itself on the rollers since the process was experimental and in no way optimized. Nevertheless, the process demonstrated that even retrograde starch formed by the more inexpensive methods described in U.S. Pat. No. 5,736,209 could be subsequently formed into thermoplastic starch when reheated in the presence of glycerin.

In addition to the foregoing examples, one could certainly modify the remaining examples of U.S. Pat. No. 5,736,209 to include glycerin in an amount sufficient to plasticize the starch binder and allow it to behave in a thermoplastic manner. Alternatively, sheets formed from starch-based mixtures that did not initially include any glycerin or other non-volatile plasticizer could be treated with glycerin after formation of the sheets in order for the glycerin to contact the starch within the sheets. Finally, to the extent that the examples do not include any inorganic filler, they could certainly be modified to include an inorganic filler in an amount within the ranges disclosed herein. In view of this, the remaining examples set forth in U.S. Pat. No. 5,736,209 are incorporated by specific reference with the understanding that the compositions disclosed therein are to be modified to include a sufficient quantity of a low volatile plasticizer and/or water to render the starch thermoplastically processible, and in addition to include an inorganic filler within the ranges disclosed herein.

Incorporated and Modified Example Set II

The modified sheets of Incorporated Example Set I are instead chopped into small pieces and then fed into an auger extruder that is able to apply sufficient heat and shear so as to create melts from the various starch-based compositions defined in Incorporated Example Set I. The thermoplastic melts are able to be shaped into a wide variety of articles using many known processes used in the thermoplastic and ceramic arts and then cooled to yield final solidified articles.

Incorporated and Modified Example Set III

The aqueous starch-based mixtures used to form the sheets set forth in each of the examples of U.S. Pat. No. 5,736,209 are modified by eliminating some or all of the water and instead including a sufficient amount of a low volatile plasticizer (such as glycerin, sorbitol, or a mixture thereof) in an amount in a range from about 3% to about 50% by weight of the starch component. An inorganic filler material is also included in an amount of at least 5% by weight of the overall compositions. These compositions are fed into the barrel of an auger extruder where they are exposed to sufficient heat and shear in order for the starch and non-volatile plasticizer to interact together to form a starch melt. The cellulosic ether also behaves in a thermoplastic manner when mixed with the starch melt under high shear so as to form a multi-component thermoplastic phase melt.

The resulting molten thermoplastic starch composition is extruded through a die into one or more continuously formed strands, which are cooled by passing the one or more strands through a cooling bath. After becoming substantially solidified, the strands are chopped into individual pieces,

such as pellets, which can be stored, transported and then further processed and shaped into a wide variety of articles by reheating the thermoplastic starch composition pellets.

Alternatively, the molten thermoplastic starch composition is directly shaped into a desired article, thus eliminating the intermediate step of forming strands and pellets.

The examples that are set forth hereinafter constitute hypothetical examples that are based upon actual mix designs that have been tested or which would be reasonably believed to be processible in a thermoplastic manner based upon actual mix designs and the knowledge learned therefrom. Although hypothetical in nature, the following examples are nonetheless to be considered to be fully enabling of thermoplastic starch compositions within the scope of the present invention.

Example 1

A thermoplastic starch composition is formed from the following components (expressed in terms of parts by weight):

starch	100 parts
glycerin	15 parts
sorbitol	15 parts
poly-ε-caprolactone	130 parts
calcium carbonate	260 parts

The starch, which comprises a native potato starch having an initial moisture content of 17% by weight, glycerin and sorbitol are blended for 1 minute within a barrel of a twin-auger extruder at a temperature of 160–180° C. in order to form thermoplastic starch melt. This melt is degassed in order to reduce the absolute moisture content to below about 5% by weight of the starch, preferably to below about 3%, and most preferably to below about 1%. Thereafter, the starch melt is blended with the poly-ε-caprolactone (PCL) for an additional minute and heated at a temperature of 170° C. in order to form a substantially homogeneous thermoplastic phase comprising thermoplastic starch and poly-ε-caprolactone. At least a portion of the thermoplastic starch (TPS) and (PCL) undergo cross-esterification to thereby form a TPS/PCL copolymer. The TPS/PCL copolymer results in a more homogeneous dispersion of the remaining TPS and PCL. The calcium carbonate is then added to the thermoplastic phase melt and mixed for a minute or less in order to form a substantially homogeneously blended inorganically filled thermoplastic starch composition. This composition is extruded through a die to form a continuous strand of material that is drawn through a cooling water bath in order to form a solidified strand, which is then chopped into individual pieces. These pieces are then reshaped as desired into any one of a variety of articles using molding techniques known in the thermoplastic industry. The articles made therefrom include approximately 50% by weight calcium carbonate, 25% poly-ε-caprolactone, and 25% thermoplastic starch. These articles were moderately stiff and exhibited properties similar to relatively stiff plastic articles known in the art.

Examples 2–19

The composition and process set forth in Example 1 are repeated except that the amount of calcium carbonate added to the thermoplastic starch composition is altered to yield compositions having the following concentrations of calcium carbonate:

Example	CaCO ₃ (wt %)	Example	CaCO ₃ (wt %)
2	5%	11	55%
3	10%	12	60%
4	15%	13	65%
5	20%	14	70%
6	25%	15	75%
7	30%	16	80%
8	35%	17	85%
9	40%	18	90%
10	45%	19	95%

As the concentration of calcium carbonate is decreased the resulting thermoplastic starch compositions have increased flexibility, tensile strength, toughness and fracture energy, but somewhat lower tensile strength. Conversely, as the concentration of calcium carbonate is increased the resulting thermoplastic starch compositions have increased stiffness, are more brittle, have somewhat increased compressive strength, but are far less expensive due to the greatly reduced materials costs. There are numerous applications in which plastics having a wide variety of mechanical properties, such as strength and stiffness, are appropriate and even desired over plastics having other strength and stiffness properties. Although the compositions having 95% by weight calcium carbonate are extremely brittle and have virtually no flexibility and minimum toughness, an example of an article that could be made therefrom is a “clay pigeon” or other frangible target used for target practice.

Examples 20–24

Thermoplastic starch compositions are formed from the following components (expressed as parts by weight).

Example	Starch	Water	Clay
20	90 parts	10 parts	10 parts
21	90 parts	10 parts	30 parts
22	80 parts	20 parts	100 parts
23	80 parts	20 parts	200 parts
24	77 parts	23 parts	500 parts

The starch that is used comprises any native starch. The starch, water and clay are blended in the barrel of an auger extruder under temperature and controlled pressure so as to form a starch melt into which is mixed the various concentrations of clay. The clay-containing starch melt is die molded into a series of disc-shaped objects. At lower concentrations of clay, the resulting disc has increased tensile strength, toughness, and fracture energy. As the amount of clay is increased, the resulting discs become more brittle and fragile but also far less expensive. Such discs could be used for a variety of purposes such as coasters to set drinks thereon, poker chips, targets, etc.

Example 25

Example 1 is repeated in every respect except that pre-dried starch having an initial water content below about 1% by weight is used instead of native starch. The resulting melt formed from the starch, plasticizer and PCL does not require significant degassing to remove excess water vapor.

Example 26

Example 1 is repeated in every respect except that a portion of the calcium carbonate is replaced with a zeolite

that is capable of scavenging water in an amount such that a substantial portion of the water initially found within the native starch is absorbed by the zeolite and thereby removed from the thermoplastic phase. This allows for a greater tendency of the starch and PCL to undergo a condensation reaction in order to form a copolymer therefrom.

Examples 27-38

Any of the foregoing examples is modified by replacing some or all of the thermoplastic polymer with one or more of the following types of polymers to form a multi-component thermoplastic phase.

Example	Polymer
27	polyethylene
28	ethylene-vinyl alcohol copolymer
29	polylactic acid
30	aliphatic-aromatic copolyester including 1,4-butanedioladipinic acid and terephthalic acid with a chain extender comprising isocyanate
31	cellulose acetate
32	cellulosic ether
33	polyester
34	polyamide
35	polyvinylpyrrolidone
36	polyacrylic acid
37	collagen
38	sunflower protein
39	sunflower protein
40	soybean protein
41	gelatin

Examples 42-47

Any of the foregoing examples are modified by including the following amounts of a fibrous component, such as a naturally occurring organic plant fiber:

Example	Fiber Concentration
42	3%
43	5%
44	10%
45	20%
46	40%
47	70%

The fibrous component is blended within the thermoplastic starch melt under conditions of sufficient shear so as to substantially homogeneously blend the individual fibers throughout the thermoplastic starch melt. This occurs prior to the addition of the inorganic filler, which is thereafter blended within the mixture at lower shear. As the fibrous component is increased, the resulting thermoplastic starch compositions have increased tensile strength, compressive strength, toughness, fracture energy, and modulus of elasticity. A wide variety of articles can be shaped from the foregoing compositions.

Examples 48-56

Any of the foregoing examples is modified such that at least a portion of the low volatile plasticizer and/or water is replaced with one or more of the following plasticizers:

Example	Plasticizer
48	propylene glycol
49	1,3-propanediol
50	neopentylglycol
51	sorbitol acetate
52	DMSO
53	polyvinyl alcohol (3-20 repeating units)
54	polyethylene glycol
55	polyglycerols (2-10 repeating units)

The concentrations of the foregoing plasticizers are adjusted in order to yield a mixture of starch and plasticizer that is able to form a melt within a temperature range from as low as 70° C. to as high as 250° C.

Example 57

Any of the foregoing examples in which the additional thermoplastic polymer has a melting point or softening range that is higher than the thermoplastic starch subcomponent will generally require additional heating to raise the temperature of the thermoplastic phase to the softening point of the additional polymer in order to form a substantially homogeneous mixture of the thermoplastic phase components.

Example 58

To any of the foregoing examples is added a cross-linking agent.

Example 59

To any of the foregoing examples is added a reactive substrate that is able to react with, or otherwise block, at least some of the hydroxyl groups along the starch polymer.

Example 60

Any appropriate combination of starch and polymer capable of forming one or more condensation reaction products with starch is processed in a manner that reduces the moisture content of the mixture to below about 0.1% of the mixture so as to promote the formation of such condensation reaction products.

Example 61

Any of the foregoing compositions is molded in a manner so as to yield a thermoplastic starch foam, such as by utilizing water as the foaming agent during a heated molding process.

VI. SUMMARY

From the foregoing, it will be appreciated that the present invention provides improved thermoplastic starch compositions and methods for manufacturing low cost, environmentally friendly sheets, films, articles made therefrom, and molded articles having appropriate mechanical properties similar to, e.g., paper, paperboard, polystyrene, plastic, metal sheets, and the like.

The present invention also disclosed how to make thermoplastic starch compositions which allow for the formation of a variety of containers and other articles using existing manufacturing equipment and techniques presently used to form articles from paper, polymer films, or moldable plastic materials.

The present invention further teaches how to manufacture environmentally friendly thermoplastic starch compositions that only include a fraction of the starch content compared to other starch-based compositions presently being utilized.

In addition, the present invention provides thermoplastic starch compositions that yield articles that are readily biodegradable and or degradable into substances commonly found on the earth.

Furthermore, the present invention provides thermoplastic starch compositions and methods which allow for the manufacture of sheets, containers and other articles at a cost that is comparable to, or even lower than, the cost of existing methods of manufacturing articles from paper, plastics, or other materials.

Moreover, the present invention provides thermoplastic starch compositions and methods which allow for the inclusion of less organic polymer materials while overcoming many of the problems associated with conventional starch melts.

The present invention further provides thermoplastic starch compositions and methods which allow for the inclusion of significant quantities of natural inorganic mineral fillers and, optionally fibrous materials, either organic or inorganic, within such thermoplastic starch compositions.

Finally, the present invention provides thermoplastic starch compositions that have improved physical properties, such as increased thermal stability, increased modulus of elasticity, compressive strength, and toughness compared to conventional thermoplastic starch compositions.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects as illustrative only and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed and desired to be secured by United States Letters Patent is:

1. A thermoplastic starch composition comprising:

a thermoplastic phase including thermoplastic starch formed by mixing and heating starch and at least one plasticizer under conditions so as to form a thermoplastic starch melt and at least one additional thermoplastic polymer blended with the thermoplastic starch; and

a solid particulate filler phase dispersed throughout the thermoplastic phase and included in an amount from about 15% to about 95% by weight of the thermoplastic starch composition.

2. A thermoplastic starch composition as defined in claim 1, wherein the plasticizer has a vapor pressure less than 1 bar when the thermoplastic phase is in a melted state.

3. A thermoplastic starch composition as defined in claim 2, wherein the plasticizer is included in an amount from about 1% to about 70% by weight of the starch and plasticizer.

4. A thermoplastic starch composition as defined in claim 2, wherein the plasticizer is included in an amount from about 5% to about 50% by weight of the starch and plasticizer.

5. A thermoplastic starch composition as defined in claim 2, wherein the plasticizer is included in an amount from about 10% to about 30% by weight of the starch and plasticizer.

6. A thermoplastic starch composition as defined in claim 2, wherein the plasticizer is at least one of ethylene glycol,

propylene glycol, glycerin, 1,3-propanediol, 1,2-butandiol, 1,3-butandiol, 1,4-butandiol, 1,5-pentandiol, 1,5-hexandiol, 1,6-hexandiol, 1,2,6-hexantriol, 1,3,5-hexantriol, neopentylglycol, sorbitol acetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate, sorbitol hexaethoxylate, sorbitol dipropoxylate, aminosorbitol, trihydroxymethylaminomethane, glucose/PEG, the reaction product of ethylene oxide with glucose, trimethylolpropane monoethoxylate, mannitol monoacetate, mannitol monoethoxylate, butyl glucoside, glucose monoethoxylate, α -methyl glucoside, the sodium salt of carboxymethylsorbitol, polyglycerol monoethoxylate, erythritol, pentaerythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol, allitol, sorbitol, polyhydric alcohols generally, esters of glycerin, DMSO, monoglycerides, diglycerides, alkylamides, polyols, trimethylolpropane, polyvinylalcohol with from 3 to 20 repeating units, or polyglycerols with from 2 to 10 repeating units.

7. A thermoplastic starch composition as defined in claim 1, wherein the plasticizer has a vapor pressure greater than 1 bar when the thermoplastic phase is in a melted state.

8. A thermoplastic starch composition as defined in claim 7, wherein the plasticizer is included in an amount in a range from about 5% to about 40% by weight of the starch and plasticizer.

9. A thermoplastic starch composition as defined in claim 7, wherein the plasticizer is selected from the group consisting of water, alcohols, aldehydes, ketones, organic acids, amines, esters, amides, imides, and mixtures thereof.

10. A thermoplastic starch composition as defined in claim 1, wherein the thermoplastic starch is melted in the presence of water and at least one plasticizer having a vapor pressure of less than 1 bar when the starch is in a melted state.

11. A thermoplastic starch composition as defined in claim 1, wherein the particulate filler is included in an amount in a range from about 5% to about 50% by volume of the thermoplastic starch composition.

12. A thermoplastic starch composition as defined in claim 1, wherein the particulate filler is included in an amount in a range from about 50% to about 90% by volume of the thermoplastic starch composition.

13. A thermoplastic starch composition as defined in claim 1, wherein the particulate filler is included in an amount greater than about 25% by weight of the thermoplastic starch composition.

14. A thermoplastic starch composition as defined in claim 1, wherein the particulate filler is included in an amount greater than about 35% by weight of the thermoplastic starch composition.

15. A thermoplastic starch composition as defined in claim 1, wherein the particulate filler is included in an amount greater than about 50% by weight of the thermoplastic starch composition.

16. A thermoplastic starch composition as defined in claim 1, wherein the solid particulate filler is at least one of sand, crushed rock, bauxite, granite, limestone, sandstone, glass beads, mica, clay, alumina, silica, fly ash, fumed silica, kaolin, glass microspheres hollow glass spheres, porous ceramic spheres, gypsum mono- and dehydrates, insoluble salts, calcium carbonate, magnesium carbonate, calcium hydroxide, calcium aluminate, magnesium carbonate, titanium dioxide, talc, ceramics, pozzolans, zirconium compounds, xonotlite, silicate gels, lightweight expanded clays, perlite, vermiculite, hydraulic cement particles, pumice, zeolites, exfoliated rock, ores, natural minerals, metallic particles, or metallic flakes.

17. A thermoplastic starch composition as defined in claim 1, wherein the at least one additional thermoplastic polymer comprises at least one polyester selected from the group consisting of aliphatic polyesters, aliphatic-aromatic copolyesters, and mixtures thereof.

18. A thermoplastic starch composition as defined in claim 1, further including a void phase dispersed throughout the thermoplastic starch composition.

19. A thermoplastic starch composition comprising:

a thermoplastic phase including thermoplastic starch formed by mixing and heating starch and at least one plasticizer under conditions so as to form a thermoplastic starch melt having a water content of less than about 5% by weight while in a melted state and prior to cooling, wherein the at least one plasticizer has a vapor pressure of less than about 1 bar when the thermoplastic phase is in melted state; and

a solid particulate filler phase dispersed throughout the thermoplastic phase and included in an amount from about 5% to about 95% by weight of the thermoplastic starch composition.

20. A thermoplastic starch composition as defined in claim 19, wherein the plasticizer is at least one of ethylene glycol, propylene glycol, glycerin, 1,3-propandiol, 1,2-butandiol, 1,3-butandiol, 1,4-butandiol, 1,5-pentandiol, 1,5-hexandiol, 1,6-hexandiol, 1,2,6-hexantriol, 1,3,5-hexantriol, neopentylglycol, sorbitol acetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate, sorbitol hexaethoxylate, sorbitol dipropoxylate, aminosorbitol, trihydroxymethylaminomethane, glucose/PEG, the reaction product of ethylene oxide with glucose, trimethylolpropane monoethoxylate, mannitol monoacetate, mannitol monoethoxylate, butyl glucoside, glucose monoethoxylate, α -methyl glucoside, the sodium salt of carboxymethylsorbitol, polyglycerol monoethoxylate, erythritol, pentaerythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol, allitol, sorbitol, polyhydric alcohols generally, esters of glycerin, DMSO, monoglycerides, diglycerides, alkylamides, polyols, trimethylolpropane, polyvinylalcohol with from 3 to 20 repeating units, or polyglycerols with from 2 to 10 repeating units.

21. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition includes from about 1% to about 6% by weight of loosely bound water after cooling with water.

22. A thermoplastic starch composition as defined in claim 19, wherein the plasticizer is included in an amount from about 1% to about 70% by weight of the starch and plasticizer.

23. A thermoplastic starch composition as defined in claim 19, wherein the plasticizer is included in an amount from about 5% to about 50% by weight of the starch and plasticizer.

24. A thermoplastic starch composition as defined in claim 19, wherein the plasticizer is included in an amount from about 10% to about 30% by weight of the starch and plasticizer.

25. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch melt initially includes a volatile plasticizing solvent having a vapor pressure greater than 1 bar, wherein at least a portion of the solvent is subsequently removed from the thermoplastic starch melt by evaporation during processing and prior to cooling and solidification of the thermoplastic starch composition.

26. A thermoplastic starch composition as defined in claim 25, wherein the volatile plasticizing solvent is selected

from the group consisting of water, alcohols, aldehydes, ketones, organic acids, amines, esters, amides, imides, and mixtures thereof.

27. A thermoplastic starch composition as defined in claim 25, wherein the volatile plasticizing solvent is initially included in an amount in a range from about 5% to about 40% by weight of the starch and solvent, wherein the solvent has a final concentration of less than about 5% by weight of the thermoplastic starch melt as a result of being removed by evaporation while the thermoplastic starch is a melted state and prior to cooling.

28. A thermoplastic starch composition as defined in claim 19, wherein the starch is derived from at least one source selected from the group consisting of corn, waxy corn, potatoes, wheat, sorghum, rice, waxy rice, tapioca, cassava, manioc, sweet potatoes, arrow root, and pith of sago palm.

29. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch is formed from native starch that initially includes its natural water content.

30. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch is formed from native starch that has been pre-dried to a water content of less than about 10% by weight.

31. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch is formed from native starch that has been pre-dried to a water content of less than about 5% by weight.

32. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch is formed from native starch that has been pre-dried to a water content of less than about 3% by weight.

33. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch melt is formed under conditions so as to have a water content of less than about 3% by weight while in a melted state and prior to cooling.

34. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch melt is formed under conditions so as to have a water content of less than about 1% by weight while in a melted state and prior to cooling.

35. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler is included in an amount from about 5% to about 50% by volume of the thermoplastic starch composition.

36. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler is included in an amount from about 50% to about 90% by volume of the thermoplastic starch composition.

37. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler is included in an amount greater than about 15% by weight of the thermoplastic starch composition.

38. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler is included in an amount greater than about 25% by weight of the thermoplastic starch composition.

39. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler is included in an amount greater than about 35% by weight of the thermoplastic starch composition.

40. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler is included in an amount greater than about 50% by weight of the thermoplastic starch composition.

41. A thermoplastic starch composition as defined in claim 19, wherein the solid particulate filler is at least one of

sand, crushed rock, bauxite, granite, limestone, sandstone, glass beads, mica, clay, alumina, silica, fly ash, fumed silica, kaolin, glass microspheres, hollow glass spheres, porous ceramic spheres, gypsum mono- and dihydrates, insoluble salts, calcium carbonate, magnesium carbonate, calcium hydroxide, calcium aluminate, magnesium carbonate, titanium dioxide, talc, ceramics, pozzolans, zirconium compounds, xonotlite, silicate gels, lightweight expanded clays, perlite, vermiculite, hydraulic cement particles, pumice, zeolites, exfoliated rock, ores, natural minerals, metallic particles, or metallic flakes.

42. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase further includes at least one additional thermoplastic polymer blended with the thermoplastic starch.

43. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer comprises a biodegradable synthetic thermoplastic polymer.

44. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer comprises a polycondensate material.

45. A thermoplastic starch composition as defined in claim 44, wherein the polycondensate material is capable of cross-condensing with at least a portion of the thermoplastic starch in order to form a condensation product between the thermoplastic starch and polycondensate material.

46. A thermoplastic starch composition as defined in claim 44, wherein the polycondensate material is selected from the group consisting of polyesters, polyamides, polyesteramides, polyimides, polylactones, polylactides, polylactams, polyethers, copolymers thereof, mixtures thereof, and derivatives thereof.

47. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer includes reactive sites that are able form a chemical bond with the thermoplastic starch.

48. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer is at least one of:

- (a) homopolymers of aliphatic or aromatic hydroxyacid monomers or their corresponding lactones or lactides;
- (b) copolymers of a first monomer of group (a) and a second monomer selected from the group consisting of
 - (i) a monomer of group (a) different from the first monomer and (ii) aliphatic or aromatic isocyanates;
- (c) block or graft copolymers between the homopolymers and copolymers selected from the groups consisting of groups (a) and (b) and one or more components selected from the group consisting of:
 - (i) cellulose, cellulose esters, and cellulosic ethers;
 - (ii) amylose, amylopectin, natural starch, and modified starches;
 - (iii) polymers derived from reaction of diols selected from the groups consisting of ethylene glycol, propylene glycol, butylene glycol, polyoxyethylene glycol, polyoxypropylene glycol, neopentyl glycol, 1,4-butanediol, cyclohexandiol, and dianhydrous sorbitol, polyester prepolymers, and polymers having diol terminal groups reacted with a substance selected from the group consisting of:
 - aromatic bifunctional isocyanates, aliphatic bifunctional isocyanates, and epoxides;
 - aliphatic dicarboxylic acids selected from the group consisting of malonic, succinic, maleic, fumaric, itaconic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids;
 - dicarboxylic cycloaliphatic acids; and

aromatic acids and aromatic anhydrides;

(iv) polyurethanes, polyamide-urethanes from diisocyanates and aminoalcohols, polyamides, polyesteramides from dicarboxylic acids and aminoalcohols, and polyester-urea from aminoacids and diesters of glycols;

(v) polyhydroxylated polymers, polyvinylalcohol, ethylene-vinylalcohol copolymers, and polysaccharides;

(vi) polyvinylpyrrolidone, polyvinylpyrrolidone-vinylacetate copolymers, and polymethacrylates;

(d) polyesters obtained from monomers or comonomers defined in groups (a) and (b) that are upgraded with chain extenders selected from the group consisting of isocyanates, epoxides, phenylesters, and aliphatic carbonates; or

(e) polyesters obtained from monomers and comonomers defined in groups (a) and (b) that are partially cross-linked by means of one or more polyfunctional acids.

49. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer is selected from the group consisting of polyesters made from 6-hydroxycaproic acid, 6-hydroxyoctanoic, 3,7-dimethyl-6-hydroxyoctanoic acid, the corresponding lactones of the foregoing, and mixtures thereof.

50. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer is an aliphatic-aromatic copolyester.

51. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer is selected from the group consisting of polyolefins, alkylsiloxanes, polyolefin adipates, polyolefin adipates, polyolefin teraphthalates, ethylenrinylaceta copolymer, vinyl resins, polystyrenes, and mixtures thereof.

52. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer includes a substantially hydrophilic thermoplastic polymer.

53. A thermoplastic starch composition as defined in claim 42, wherein the additional thermoplastic polymer is selected from the group consisting of proteins, cellulose-based materials, polysaccharide gums, polymers derived from plants, animals, and animal products, and mixtures thereof.

54. A thermoplastic starch composition as defined in claim 42, wherein the ratio of thermoplastic starch to additional thermoplastic polymer is in a range from about 1:9 to about 9:1.

55. A thermoplastic starch composition as defined in claim 42, wherein the ratio of thermoplastic starch to additional thermoplastic polymer is in a range from about 2:8 to about 8:2.

56. A thermoplastic starch composition as defined in claim 42, wherein the ratio of thermoplastic starch to additional thermoplastic polymer is in a range from about 3:7 to about 7:3.

57. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase further includes a thermosetting resin.

58. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase further includes a cross-linking agent.

59. A thermoplastic starch composition as defined in claim 58, wherein the cross-linking agent is selected from the group of polyacids, polyamines, anhydrides, and derivatives of the foregoing.

60. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase further includes

a reactive component that is capable of reacting with hydroxyl groups of the thermoplastic starch.

61. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition further includes an admixture selected from the group consisting of lubricants, dispersants, humectants, waterproofing agents, phase mediators, softeners, mold release agents, flexibilizers, and blending enhancers.

62. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase has a concentration in a range from about 10% to about 90% by volume of the thermoplastic starch composition.

63. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase has a concentration in a range from about 20% to about 80% by volume of the thermoplastic starch composition.

64. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase has a concentration in a range from about 30% to about 70% by volume of the thermoplastic starch composition.

65. A thermoplastic starch composition as defined in claim 19, farther including a fibrous phase comprising individual fibers having an aspect ratio greater than about 10:1 and dispersed throughout the thermoplastic phase in an amount of up to about 90% by weight of the thermoplastic starch composition.

66. A thermoplastic starch composition as defined in claim 65, wherein the individual fibers have an aspect ratio greater than about 25:1.

67. A thermoplastic starch composition as defined in claim 65, wherein the individual fibers have a length in a range from about 0.1 mm to about 2 mm.

68. A thermoplastic starch composition as defined in claim 65, wherein the individual fibers have a length greater than about 2 mm.

69. A thermoplastic starch composition as defined in claim 65, wherein the fibrous phase comprises inorganic fibers selected from the group consisting of glass fibers, graphite fibers, silica fibers, ceramic fibers, rock wool fibers, metal fibers, and mixtures thereof.

70. A thermoplastic starch composition as defined in claim 65, wherein the fibrous phase comprises organic fibers selected from the group consisting of plant derived fibers, cotton, hard wood fibers, softwood fibers, flax, abaca, sisal, ramie, hemp, bagasse, recycled paper fibers, polymer fibers, and mixtures thereof.

71. A thermoplastic starch composition as defined in claim 65, wherein the fibrous phase is included in an amount in a range from about 3% to about 80% by weight of the thermoplastic starch composition.

72. A thermoplastic starch composition as defined in claim 65, wherein the fibrous phase is included in an amount in a range from about 5% to about 60% by weight of the thermoplastic starch composition.

73. A thermoplastic starch composition as defined in claim 65, wherein the fibrous phase is included in an amount in a range from about 10% to about 30% by weight of the thermoplastic starch composition.

74. A thermoplastic starch composition as defined in claim 19, wherein the particulate filler comprises an organic filler.

75. A thermoplastic starch composition as defined in claim 74, wherein the organic filler is at least one of sawdust, wood flour, bran, or wood flakes.

76. A thermoplastic starch composition as defined in claim 19, further including a phase comprising discrete organic globules of at least partially melted organic filler.

77. A thermoplastic starch composition as defined in claim 19, further including a discontinuous phase of substantially nonagglomerated voids dispersed throughout the thermoplastic phase.

78. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is in the form of a molten material capable of being shaped into a desired article of manufacture and then substantially solidified by cooling to below its melting point or range.

79. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is in the form of a solidified granulate or other intermediate form that is capable of being remelted as a thermoplastic material and reshaped into a desired article of manufacture.

80. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is formed into a film having a thickness in a range from about 1 micron to about 1 mm.

81. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is formed into a film having a thickness in a range from about 0.001 mm to about 1 cm.

82. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is formed into a molded article having a wall thickness in a range from about 0.1 mm to about 10 cm.

83. A thermoplastic starch composition as defined in claim 19, wherein at least the thermoplastic phase of the thermoplastic starch composition is biodegradable.

84. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase of the thermoplastic starch composition is impermeable to water.

85. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic phase of the thermoplastic starch composition is degradable in water.

86. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is formed into a film or sheet and has been stretched after initial formation in at least one direction.

87. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch has a crystallinity of less than about 5%.

88. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition has a melting point or range from about 70° C. to about 240° C.

89. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition has a melting point or range from about 80° C. to about 220° C.

90. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition has a melting point or range from about 100° C. to about 200° C.

91. A thermoplastic starch composition as defined in claim 19, wherein the thermoplastic starch composition is formed into a laminate coating applied to a substrate.

92. A thermoplastic starch composition comprising:
a thermoplastic phase including a mixture of thermoplastic starch and at least one additional thermoplastic polymer, wherein the thermoplastic starch is formed by mixing and heating starch and at least one plasticizer under conditions so as to form a thermoplastic starch melt and so that at least a portion of the thermoplastic starch melt forms at least one condensation product with the at least one additional thermoplastic polymer;
a solid particulate filler phase dispersed throughout the thermoplastic phase and included in an amount from about 5% to about 95% by weight of the thermoplastic starch composition.

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93. A thermoplastic starch composition as defined in claim 92, wherein the additional thermoplastic polymer is at least one member selected from the group consisting of polyester, polyesteramides, and derivatives thereof.

94. A thermoplastic starch composition comprising:

a thermoplastic phase including thermoplastic starch formed by mixing and heating starch and at least one plasticizer under conditions so as to form a thermoplastic starch melt;

a solid particulate filler phase dispersed throughout the thermoplastic phase and included in an amount from about 5% to about 95% by weight of the thermoplastic starch composition; and

a fibrous phase dispersed throughout the thermoplastic phase and comprising individual fiber in a concentration of from about 3% to about 70% by weight of the thermoplastic starch composition.

95. A thermoplastic starch composition as defined in claim 94, wherein the thermoplastic phase further includes

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at least one biodegradable hydrophobic synthetic polymer blended with the thermoplastic starch.

96. An inorganically filled, destructureized starch composition comprising:

(a) a thermoplastic phase including destructureized starch and at least one additional polymer, wherein the destructureized starch is formed by mixing and heating starch with water under conditions so as to form a destructureized starch melt having a water concentration in a range from about 5% to about 40% by weight of the starch and water, wherein the destructureized starch and additional thermoplastic polymer are substantially homogeneously blended together; and

a solid particulate inorganic filler phase dispersed throughout the thermoplastic phase and included in an amount greater than about 15% by weight of the destructureized starch composition.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,231,970 B1
DATED : May 15, 2001
INVENTOR(S) : Per Just Andersen, Simon K. Hodson and Harald Schmidt

Page 1 of 3

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,

Item [75], Inventors, insert -- **Harald Schmidt**, of Emmerich, Germany --

ABSTRACT,

Line 3, after "component" insert -- . --

Column 1,

Line 45, change "containers" to -- containers) --

Column 3,

Line 39, after "resulting" insert -- gelatinization or melting point of the starch) and it must be somewhat polar in order to be --

Column 4,

Line 11, change "et al;" to -- et al.; --

Line 34, before "removed" insert -- be --

Lines 42-43, change "L örcks" to -- Lörcks --

Column 5,

Line 37, change "paper." to -- paper, --

Column 6,

Line 30, after "melt" insert -- . --

Line 31, after "with" change "on," to -- one --

Column 8,

Line 48, change "fiber;" to -- fibers --

Column 11,

Line 41, after "reinforcement" insert -- , --

Column 12,

Line 5, before "fact" insert -- the --

Line 24, change "The" to -- the --

Column 13,

Line 23, after ' "flowable" ' insert -- on the other. --

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,231,970 B1
DATED : May 15, 2001
INVENTOR(S) : Per Just Andersen, Simon K. Hodson and Harald Schmidt

Page 2 of 3

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 14,

Line 9, after "transition" delete [,]
Line 12, change "polymer" to -- polymers --
Line 38, delete [generally]

Column 17,

Line 35, after "phases" delete [,]
Line 38, change "phase" to -- phases --
Line 53, after "phases" change "is" to -- are --

Column 18,

Line 47, change "Theologically" to -- rheologically --

Column 19,

Line 38, change "particular" to -- particularly --
Line 61, after "added" insert -- to --

Column 20,

Line 14, change "predried" to -- pre-dried --
Line 33, before "concentration" insert -- a --

Column 22,

Line 2, before "polymers" insert -- more --
Line 33, after "to" insert -- be --

Column 23,

Lines 5, 7 and 8, change " $\text{cm}^3/2$ " to -- $\text{cm}^{-3/2}$ --
Line 20, change "tee" to -- the --
Line 38, change "more slow" to -- slower --

Column 24,

Line 23, after "blend" insert -- of --

Column 29,

Line 46, change "Similar," to -- Similarly, --
Line 48, change "allow" to -- allows --

Column 30,

Line 52, before "the" insert -- of --

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,231,970 B1
DATED : May 15, 2001
INVENTOR(S) : Per Just Andersen, Simon K. Hodson and Harald Schmidt

Page 3 of 3

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 36,

Line 65, change "Theological" to -- rheological --

Column 39,

Line 19, change "in art" to -- in the art --

Column 41,

Line 6, change "present" to -- presence --

Column 42,

Line 30, before "comprises" delete [will]

Column 51,

Line 13, change "filly" to -- fully --

Column 58,

Line 10, change "is a" to -- is in a --

Column 59,

Line 35, after "able" insert -- to --

Column 60,

Line 32, delete the second occurrence of [polyolefin adipates,]

Signed and Sealed this

Ninth Day of July, 2002

Attest:

A handwritten signature in black ink, appearing to read "James E. Rogan", with a horizontal line drawn underneath it.

Attesting Officer

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

EXHIBIT G

United States Patent [19]
Chinnaswamy et al.

[11] **Patent Number:** **5,496,895**
 [45] **Date of Patent:** **Mar. 5, 1996**

[54] **BIODEGRADABLE POLYMERS**

[75] **Inventors:** **Rangaswamy Chinnaswamy; Milford A. Hanna**, both of Lincoln, Nebr.

[73] **Assignee:** **The Board of Regents of the University of Nebraska**, Lincoln, Nebr.

[21] **Appl. No.:** **942,132**

[22] **Filed:** **Sep. 8, 1992**

Related U.S. Application Data

[63] Continuation of Ser. No. 393,373, Aug. 14, 1989, abandoned.

[51] **Int. Cl.⁶** **C08G 63/48; C08G 63/91; C08F 8/00; C08F 32/00**

[52] **U.S. Cl.** **525/54.2; 525/54.3; 525/326.1; 525/374; 525/379; 525/380; 525/382; 527/300**

[58] **Field of Search** **525/54.2, 54.3, 525/326.1, 374, 379, 380, 382; 527/300**

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,451,629 5/1984 Tanaka et al. 526/238.23

4,891,404 1/1990 Narayan et al. 525/54.2

Primary Examiner—Nathan M. Nutter

Attorney, Agent, or Firm—Vincent L. Carney

[57] **ABSTRACT**

To prepare a biodegradable plastic, biodegradable materials such as starches and a non-biodegradable polymer such as a polystyrene, polyurethane, polyethylene, polypropylene, or polycarbonate are treated: (1) under heat, pressure and reagents to break the polymers; and (2) by adding to them an oxidizing agent. This treatment forms and/or makes available reactive groups for bonding: (1) on the biodegradable material groups such as aldehyde or hydroxyl groups in the case of the carbohydrates and amine groups in the case of proteins and certain other compounds such as urea; and (2) on the non-biodegradable plastic groups such as aldehydes, methyl, propyl, ethyl, benzyl or hydroxyl groups. In one embodiment, plastic and starch are processed in an extruder by: (1) mixing a starch in a range of between 15 percent and 80 percent, an oxidizing agent and an agent to break up the starch and the plastics; and (2) subjecting the combination to sufficient heat and/or pressure to break the plastic into shorter chains and bond monosaccharides to monomers from the non-biodegradable polymer.

4 Claims, No Drawings

BIODEGRADABLE POLYMERS

This application is a continuation of application Ser. No. 07/393,373, filed Aug. 14, 1989, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to biodegradable polymers and to methods of making them from non-biodegradable polymers such as petroleum-based plastics combined with other biodegradable polymers, such as for example, carbohydrates, proteins, lipids or the like.

It is known to alter polymers such as petroleum-based plastics by the incorporation of some carbohydrates to increase their biodegradability. One prior art biodegradable polymer and method of making it is disclosed in U.S. Pat. No. 4,016,117 to Griffin, issued Apr. 5, 1977. In this product, a synthetic resin incorporates particles of biodegradable substances and an auto-oxidizable substance. The processing preserves the starch granules in the final product. This polymer, when it contacts a transition metallic salt, auto-oxidizes to generate a peroxide or a hydroperoxide.

Other biodegradable products are disclosed in U.S. Pat. Nos. 4,405,731 to Carter issued Sep. 20, 1983; 3,778,392 to Hughes issued Dec. 11, 1973; 3,949,145 to Otey et al. issued Apr. 6, 1979; and 4,280,920 to Kesting.

The biodegradable plastics disclosed in these United States patents have the disadvantages of only containing from approximately 5 percent to 15 percent carbohydrate while retaining its characteristics as a plastic although they may have up to 50 percent starch but become paperlike at such high levels and lose the typical characteristics of thermoplastic or thermosetting plastics. The altered structure reduces the elasticity and shear strength.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide a novel biodegradable polymer.

It is a further object of the invention to provide a novel process for making biodegradable polymers.

It is a still further object of the invention to provide a novel biodegradable polymer in which a carbohydrate or protein or possibly lipids may be substituted in percentages between 15 percent and 80 percent while preserving a substantial number of the desirable properties of the polymer.

It is a still further object of the invention to make a novel biodegradable polymer using a process which causes chemical modification of a carbohydrate or protein or possibly lipids or urea and a non-biodegradable polymer to make a biodegradable polymer.

It is a still further object of the invention to provide a novel biodegradable plastic and process for incorporating carbohydrates or proteins or possibly lipids into polystyrene, polyurethane, polyethylene, polypropylene, or polycarbonate plastics in quantities greater than 15 percent while preserving many of the functional characteristics of the plastic.

It is a still further object of the invention to provide a novel foam plastic product and method of making it.

It is a still further object of the invention to provide a novel film plastic product and method of making it.

In accordance with the above and further objects of the invention, a biodegradable polymer is provided having polymeric chains that include both hydrocarbon monomers

from a non-biodegradable polymer and other biodegradable groups such as monosaccharides or amino acids or the like that render the polymer biodegradable. In these polymers, the biodegradable groups and hydrocarbon monomers are bonded or interconnected by single and/or double bond covalent linkages, hydrocarbon or bridge bonds, Van der Waals' forces or the like to each other. The biodegradable groups may be obtained from carbohydrates, proteins, lipids, urea or other materials that can result in groups that combine with the hydrocarbon monomers from the plastic while retaining biodegradability.

In preparing the biodegradable plastic, the biodegradable group and a non-biodegradable polymer such as a polystyrene, polyurethane, polyethylene, polypropylene, or polycarbonate are treated: (1) under heat, pressure and reagents to break the polymers; and (2) by adding to them an oxidizing agent. This treatment forms and/or makes available reactive groups for bonding: (1) on the biodegradable material such as aldehyde or hydroxyl groups in the case of the carbohydrates and amine groups in the case of proteins and certain other compounds such as urea; and (2) on the non-biodegradable polymers such as aldehydes, methyl, propyl, ethyl, benzyl or hydroxyl groups.

In one embodiment, the non-biodegradable polymer is treated by: (1) adding to it a carbohydrate in a range of between 15 percent and 80 percent, an oxidizing agent and an agent to break up the starch or similar carbohydrates; and (2) subjecting the combination to sufficient heat and/or pressure to break the polymer into shorter chains and bond monosaccharides to monomers from the non-biodegradable polymer.

In one example of this embodiment, the non-biodegradable polymer is polystyrene, the oxidizing agent is citric acid and the substance for degrading the starch is sodium bicarbonate. The heat and pressure is provided by extruding the combination at high temperatures to form a biodegradable foam plastic in which the sodium bicarbonate and citric acid: (1) release carbon dioxide as a foaming agent; (2) oxidize the methyl groups of the styrene to form groups such as aldehyde groups which react with groups on the starch; and (3) form sodium hydroxide to degrade the starch and thus to form aldehydes such as formaldehyde or hydroxyl groups to react with the styrene. Similarly, proteins can be degraded to amino acids or aldehyde compounds having reactive amine or carboxyl groups to react with the hydroxyl or aldehyde groups of the oxidized carbohydrate.

As can be understood from the above description, the biodegradable polymer of this invention and the method of making it have several advantages, such as for example: (1) the biodegradable polymer retains its physical characteristics with a large percentage of carbohydrate added or protein or other biodegradable material; (2) the biodegradable polymer effectively degrades when discarded; (3) the process permits the inclusion of a large amount of carbohydrate; and (4) the biodegradable polymer is less expensive than other biodegradable polymers.

DETAILED DESCRIPTION

A carbohydrate, protein or lipid substituted biodegradable polymer or other substituted biodegradable polymer such as a urea substituted biodegradable polymer includes a polymeric chain including both hydrocarbon monomers such as alkyne and alkene polymers derived from petroleum and biodegradable monomers, such as amino acids or monosaccharides or lipids, preferably obtained from agricultural

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products, such as wheat or corn, in a molecule. The hydrocarbon monomers and monosaccharides or amino acids or other such groups are covalently bound to each other.

More specifically, the monosaccharides or amino groups or carboxyl groups of lipids are bound in groups or chains of units or as a single monomer side-chains or branches of the feedstock to hydrocarbon polymers and/or within the hydrocarbon chain to pairs of monomers such as glucose, styrene, ethylene, benzyl, acetyl (for lipids) and amino acids. The monosaccharide, amino or carboxyl groups or group are bonded to hydrocarbon monomers from the feedstock non-biodegradable polymer and similarly the hydrocarbon monomers from the feedstock non-biodegradable polymer may be connected as single monomers to monosaccharides or amino acids or the like or be bonded as chains of hydrocarbon monomers. The different types of monomers are distributed throughout the polymer molecules of the biodegradable polymer. The monomers originating from the petroleum based polymer and from the biodegradable carbohydrate, protein, lipid or urea may be interconnected by single and/or double bond covalent linkages, hydrocarbon or bridge bonds, Van der Waals' forces or the like but most commonly by covalent bonds.

The biodegradable polymers are prepared by a high-temperature short-time, high-shear extrusion process in which one or more biodegradable material such as carbohydrate or protein or lipid or urea or the like and one or more non-biodegradable polymer such as petroleum based plastics are mixed with an oxidizing agent and a mild acid or alkali that breaks the biodegradable polymer into chains of between 1,000 to 100,000 daltons or approximately 500 to 50,000 monosaccharide groups in the case of starch or other carbohydrates or the equivalent length in proteins or lipids.

The non-biodegradable polymer may be any alkyne or alkene chain with a substituted methyl and/or other functional groups such as ethene, ethyne, propylene, propyne, butadiene and the like groups on plastics such as polystyrene, polyurethane, polyethylene, polypropylene, and polycarbonate among others. The proportion of amino acid or carbohydrate to non-degradable polymer w/w (weight to weight) is between 15 and 80 percent carbohydrate or amino acid and the carbohydrate, protein or starch should have a chain length greater than 1,000 daltons.

Suitable compounds that degrade the carbohydrates include sodium hydroxide, citric acid, sodium chloride, sodium bisulfite, urea, acrylic acid, acrylonitrile, adipic acid, aluminum trichloride, amino resins, analeic acid, phthalic acid, azo-bis-isobutyronitrile, berleculite, benzoyl peroxide, bisphenol A, boron trifluoride, butadiene, casein, cellophate, acetate, butyrate, triacetate, tanthate, chloroprenyl, decamethylene glycol, diethyl maleate, diethyl phthalate, ethylene glycol, propylene glycol, epichlorohydrin, epoxy resins, ethane, ethylene, ethylene oxide, formaldehyde, fumaric acid, glycerol, hemomethylene diamine, hexamine, isobutene, isobutylene, melamine, methacrylic acid, methyl vinyl acetone, polyethylene terephthalate, phenol, polyamides, potassium amide, sebacoyl chloride, sodium naphthalide, styrene, titanium tetrachloride, vinyl chloride, vinyl sulphonic acid, ziegler catalyst.

Compounds for degrading carbohydrates are known in the art and differ from each other in their reactions with starch in known ways. Instead of a compound that degrades carbohydrates, compounds that form such carbohydrate-degrading compounds, such as sodium bicarbonate and citric acid, may also be used.

In manufacturing one suitable biodegradable polymer, a carbohydrate such as starch and non-biodegradable polymer

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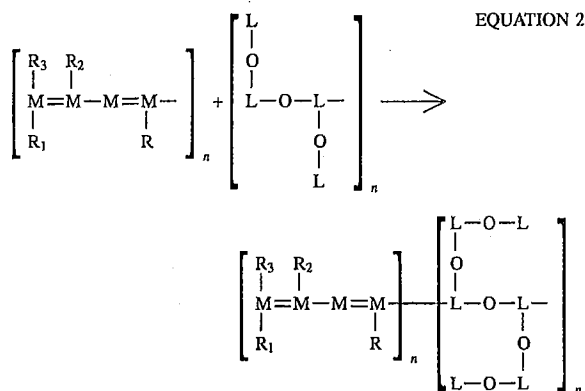
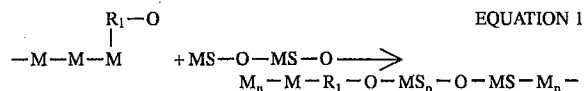
are combined in a range of weight-to-weight ratios from approximately 4 parts non-biodegradable polymer to one part carbohydrates at one end to one part non-biodegradable polymer to two parts carbohydrate at the other end of the range and with 1 to 10 percent each of an oxidizing agent and carbohydrate degrader, and in some embodiments, a foaming agent. The combination is subjected to heat at a selected temperature falling within the range of 110 to 180 degrees Centigrade and a selected pressure falling within the range of 3 to 55 mega-Pascals.

As a result of this process, the carbohydrate molecules degrade and then react with the non-biodegradable polymer molecules to form a new polymer having interconnected chemical groups from the carbohydrate and from the original non-biodegradable polymer. The reaction under these conditions is believed to be as shown in equation 1.

In the reaction of equation 1: MS indicates any monosaccharide or amino or lipid group; R1 is any group attached to the alkyl group of a monomer of the non-biodegradable polymer; and M is any unit or monomer of the basic feedstock non-biodegradable polymer.

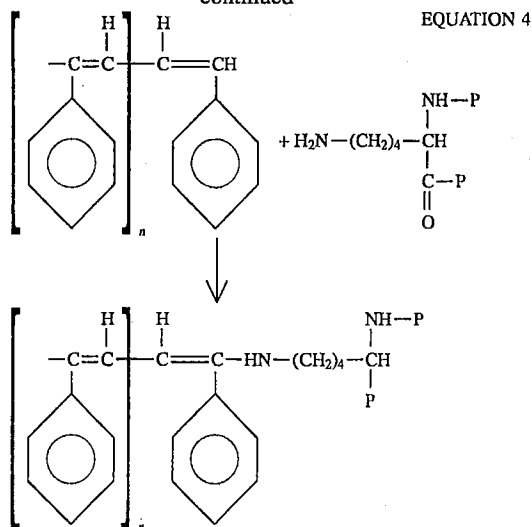
In equation 2, there is shown a general reaction between a carbohydrate and a non-biodegradable petroleum-based polymer. In this equation, L represents any carbohydrate monomer, M is a monomer of the non-biodegradable polymer such as polystyrene, polyethylene or the like and R1, R2, R3 are any other hydrocarbon group such as for example any acetyl, methyl, propyl, butyl or the like. Proteins or amino acids and probably lipids may be substituted into non-biodegradable polymers to further increase the degradability.

For example, as shown in equation 4 a protein or amino acid, shown as P with connected reactive groups, can react with polystyrene or other non-biodegradable polymer have n monomers to obtain the biodegradable polymer and as shown in equation 5, a lipid, shown as F with a reactant group is combined with a non-biodegradable polymer having n monomers M



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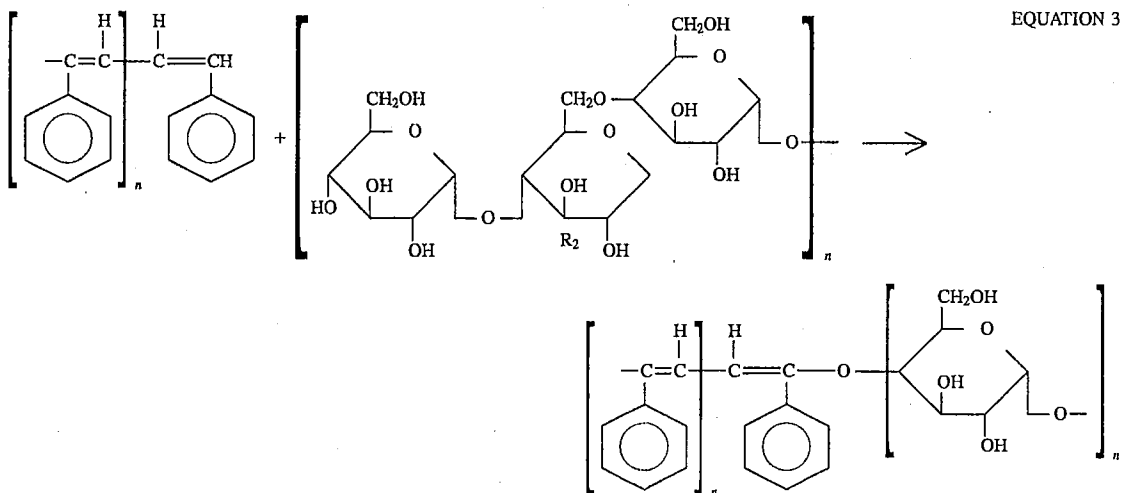
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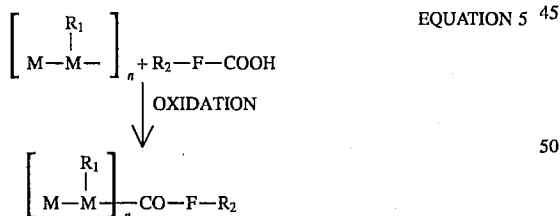
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tially degraded and has lost its mechanical strength or, if it has not reached that stage, that there has been an increase in microbial growth on the material of at least four times the starting growth. It should loose at least 50 percent of its physical integrity and strength within six months in a landfill.

Also biodegradable polymer in this specification includes those polymers that are



-continued



and a reactive group R1 or R2 either of which may be a carboxyl group to obtain a biodegradable polymer.

In this specification, the term "non-biodegradable" means a material, which when incubated at room temperature and 50 percent humidity for a time period of two months, shows no substantial growth of bacteria or fungi nor an increase of less than a multiple of 4 in bacteria or fungi if the initial product already contained some growth. It should suffer less than 50 percent loss of its integrity and physical strength by conversion of the polymer to carbon dioxide and lower molecular weight hydrocarbons within six months in a landfill. In this specification, the term "biodegradable material" means that after incubation at a moisture of 50 percent at room temperature for two months, the material is substan-

degradable through a process by which fungi or bacteria secretes enzymes to convert a complex molecular structure of the compound to simple gasses and organic compounds and compounds capable of decomposing or deteriorating through a natural chemical process into harmless components after exposure to natural elements for not more than one year.

In the preferred embodiment, a starch based biodegradable polymer is prepared by a high-temperature short-time, high shear extrusion processes. Starch and polystyrene are combined in a ratio of 60 percent to 40 percent and with 1 to 10 percent each of citric acid and sodium bicarbonate when extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The starch molecules degrade and then react with polystyrene molecules to form a network. The citric acid controls the molecular degradation and interactions. The sodium bicarbonate decomposes to NaOH and CO₂. The NaOH degrades the starch molecules and the CO₂ contributes to the uniform foam structure of the product. A reaction under these conditions is believed to be illustrated as shown in equation 3 in which the left-hand top formula is that of a polystyrene, the top right formula is that of a starch and the

bottom formula is the formula of the new biodegradable polystyrene.

The process of choice appears to be high-temperature short-time extrusion. This process, including the steps for forming containers is described in "Foam, Extruded Polystyrene", *Encyclopedia of Packaging Technology* by Bakker, copyright 1986, published by John Wiley & Sons, Inc, N.Y. N.Y., USA, page 345, the disclosure of which is incorporated herein by reference. However, techniques such as thermosetting, injection molding and dispersion pressurized reactors may also provide satisfactory reaction conditions to form a similar starch-polystyrene network.

The resultant product may find use as meat trays, cups, egg cartons, plates, bowls, loose-fill packaging materials, insulation and sound proofing materials. In other words, it can be used in areas where expanded plastics are currently being used. Moreover, other plastic products such as bottles and wrapping materials, may be made using corresponding non-biodegradable plastics as a feedstock. For some uses a rodenticide or repellent and an insecticide or repellent or antimicrobial agents may be included.

The invention is illustrated by the following examples:

EXAMPLES

GENERAL

The temperatures and pressures in the examples are applied during extrusion of the combination of ingredients. The starch in the actual examples was obtained from corn and wheat but can also be obtained from sorghum, potato, rice and tapioca.

EXAMPLE 1

Wheat starch and polystyrene are mixed in a ratio of 66 percent wheat starch by weight to 27 percent polystyrene and combined with 3 percent citric acid and 6 percent sodium bicarbonate. They are extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The resulting product has the appearance of the original expanded polystyrene.

EXAMPLE 2

Wheat starch and polystyrene are mixed in a ratio of 38.1 percent wheat starch by weight to 57.1 percent polystyrene and combined with 1.6 percent citric acid and 3.2 percent sodium bicarbonate. They are extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The resulting product has the appearance of the original expanded polystyrene.

EXAMPLE 3

Wheat starch and polystyrene are mixed in a ratio of 52.9 percent wheat starch by weight to 35.3 percent polystyrene and combined with 4.4 percent citric acid and 7.4 percent sodium bicarbonate. They are extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The resulting product has the appearance of the original expanded polystyrene.

EXAMPLE 4

Wheat starch and polystyrene are mixed in a ratio of 23.4 percent wheat starch by weight to 70.3 percent polystyrene and combined with 1.6 percent citric acid and 4.7 percent sodium bicarbonate. They are extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The resulting product has the appearance of the original expanded polystyrene.

EXAMPLE 5

One percent milk protein and 20 percent corn starch and/or wheat starch are combined with 79 percent polystyrene, 1.6 percent citric acid and 4.7 percent sodium bicarbonate. They are extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The resulting product has the appearance of the original expanded polystyrene.

EXAMPLE 6

One percent wheat protein (isolated) and 20 percent corn starch and/or wheat starch are combined with 79 percent polystyrene combined with 1.6 percent citric acid and 4.7 percent sodium bicarbonate. They are extrusion-cooked at a temperature of 140 degrees Centigrade and a pressure of approximately 20 mega-Pascals.

The resulting product has the appearance of the original expanded polystyrene.

As can be understood from the above description, the biodegradable polymer of this invention and the method of making it have several advantages, such as for example: (1) the biodegradable polymer is less expensive than other biodegradable polymers; (2) the biodegradable polymer retains its physical characteristics with a large percentage of carbohydrate added; (3) the biodegradable polymer effectively degrades when discarded; and (4) the process permits the inclusion of a larger amount of carbohydrate.

Although a preferred embodiment of the invention has been described with some particularity, many modification and variations in the preferred embodiment may be made without deviating from the invention. Accordingly, it is to be understood that, within the scope of the appended claims, the invention may be practiced other than as specifically described.

What is claimed is:

1. A biodegradable polymer comprising polymeric chains that include both monosaccharides from a starch feedstock and hydrocarbon monomers from a feedstock non-biodegradable plastic covalently bound to each other in ratios by weight of between 15 and 80 percent monosaccharide from starch feedstock to hydrocarbon from the feedstock non-biodegradable plastic, wherein at least some of the monosaccharides are bound by covalent bonds within the hydrocarbon chain of the biodegradable polymer.

2. A method of making a biodegradable polymer comprising the steps of: combining a carbohydrate and a non-biodegradable polymer with material that breaks up the carbohydrate and causing a reaction under heat and pressure which substitutes at least some monosaccharide groups from the carbohydrate into the non-biodegradable polymer chain wherein the percentage by weight of substituted carbohydrate to non-biodegradable polymer is between 15 to 80 percent.

3. A process according to claim 2 wherein the non-biodegradable polymer is a polystyrene and the carbohydrate is a starch.

4. A method of making a biodegradable polymer comprising the steps of: combining a carbohydrate and non-biodegradable polymer with material that breaks up the carbohydrate and causing a reaction under heat and pressure which substitutes at least some monosaccharide groups from the carbohydrate into the non-biodegradable polymer chain wherein the percentage by weight of substituted carbohydrate to non-biodegradable polymer is between 15 to 80 percent;

the non-biodegradable polymer is a polystyrene and the carbohydrate is a starch;

the combination is injection molded in a dispersion pressurized reactor; the carbohydrate to polystyrene ratio is 60 percent to 40 percent and includes 10 to 20 grams of citric acid and sodium bicarbonate and is extrusion processed at a temperature of substantially 140 degrees Centigrade and a pressure of approximately 20 megapascals.

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EXHIBIT H

- [54] **IMPACT RESISTANT POLYBLENDS OF
POLYAMIDES, ACID COPOLYMERS AND
ANHYDRIDE FUNCTIONALIZED
ELASTOMERS**
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Chester, Pa.
- [73] Assignee: Arco Chemical Technology, L.P.,
Wilmington, Del.
- [21] Appl. No.: 518,898
- [22] Filed: May 4, 1990
- [51] Int. Cl.⁵ C08L 77/00
- [52] U.S. Cl. 525/66; 525/179
- [58] Field of Search 525/66, 179

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4,429,076	1/1984	Saito et al.	525/57
4,528,326	7/1985	Dean	525/66
4,593,066	6/1986	Dean	525/66
4,657,970	4/1987	Shiraki et al.	525/57
4,777,211	10/1988	Lavingood et al.	525/66
4,795,782	1/1989	Lutz et al.	525/66

FOREIGN PATENT DOCUMENTS

277381	10/1988	European Pat. Off.
3604348	8/1987	Fed. Rep. of Germany
3604376	8/1987	Fed. Rep. of Germany
56-112957	9/1981	Japan
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Primary Examiner—Ana L. Carrillo
Attorney, Agent, or Firm—Stephen D. Harper

[57] **ABSTRACT**

Moldable multi-phase polyblends having excellent impact properties are disclosed which comprise blends of a polyamide, a thermoplastic copolymer of an α,β -unsaturated carboxylic acid and a monovinyl aromatic monomer, and an anhydride-functionalized elastomer. The functionalized elastomers are low in unsaturation, providing polyblends having good oxidative stability, and are α,β -carboxylic acid anhydride adducts of EPDM-type rubbers, hydrogenated block or random copolymers of monovinyl aromatic monomers and conjugated dienes, or hydrogenated polymers of conjugated dienes. Optimum impact properties are achieved by combining the components of the polyblends using particular melt-blending procedures.

8 Claims, No Drawings

IMPACT RESISTANT POLYBLENDS OF POLYAMIDES, ACID COPOLYMERS AND ANHYDRIDE FUNCTIONALIZED ELASTOMERS

BACKGROUND OF THE INVENTION

This invention is directed to multi-phase polyblends of polyamide resins, high molecular weight thermoplastic copolymers containing unsaturated carboxylic acid, and adducts of carboxylic acid anhydrides and elastomeric polymers. The invention additionally relates to a method for the preparation of such thermoplastic moldable polymer blends wherein chemical grafting of the blend components is accomplished.

Polyamide resins have been widely used as thermoplastics in molding applications because of their high resistance to chemicals, heat, and abrasion and their generally good mechanical properties. However, polyamide resins possess certain deficiencies, including shrinkage during molding and high hygroscopicity. The tendency to absorb water results in dimensional stability problems and loss of mechanical strength. Although polyamide resins are fairly tough under most impact conditions, they can be notch-sensitive and brittle at low temperatures. Polyamide resins have been blended with other polymers to compensate for these deficiencies or to enhance mechanical properties such as stiffness and tensile strength.

U.S. Pat. No. 4,528,326 teaches polyblends of polyamide resins having at least seven methylene units separating each amide functional group and rubber-modified styrene/unsaturated carboxylic acid anhydride or imide copolymer resins. Polyblends of polyamides containing fewer than seven methylene units were found to have undesirably low impact strength.

Jpn. Pat. No. 56-112957 teaches polyblends of polyamide resins and rubber-modified styrene copolymer containing high levels of unsaturated carboxylic acid anhydride, with the styrene copolymer preferably also containing an unsaturated carboxylic acid ester in order to minimize the extent of undesired cross-linking during melt-kneading.

U.S. Pat. No. 4,421,892 contains similar teachings regarding polyblends of polyamide resins and styrene copolymers containing high levels of unsaturated carboxylic acid anhydride. Good mechanical strength was only achieved in such polyblends when an unsaturated carboxylic acid ester was additionally present in the styrene copolymer.

Jpn. Pat. No. 57-025355 teaches blends of styrene/maleic anhydride copolymers and polyamides, but does not teach how adequate impact properties may be accomplished with such blends.

Ger. Pat. No. 3,604,348 teaches blends of polyamides, ethylene/acrylate or acrylic acid copolymers, and styrene/acrylic acid or styrene/anhydride copolymers. Similar teachings are found in Ger. Pat. No. 3,604,376 which additionally discloses the use of a conjugated diene polymer or copolymer to improve the impact strength of such blends.

U.S. Pat. No. 4,174,358 teaches the toughening of polyamides by blending with elastomeric polymers bearing functional groups, including anhydride, which may chemically react with the polyamide so as to achieve grafting between the components.

U.S. Pat. No. 4,427,828 teaches the impact modification of polyamides with maleic anhydride adducts of either a hydrogenated polymer of a conjugated diene or

a hydrogenated block or random copolymer of a copolymer of a conjugated diene and a monovinyl aromatic monomer.

SUMMARY OF THE INVENTION

In contrast to prior art blends of polyamides and styrene copolymers, the multi-phase polyblends of this invention have an excellent balance of properties. These outstanding properties are obtained without the use of an unsaturated carboxylic acid ester as a third comonomer in the styrene copolymer or a limitation on the type of polyamide resin employed.

The multi-phase polyblends of the present invention exhibit superior stiffness and impact strength and less absorption of moisture relative to the unblended polyamide resins. At the same time, these polyblends retain the other desirable properties of polyamide resins, including high tensile strength and chemical, heat, and abrasion resistance.

It is an object of this invention to obtain moldable multi-phase polyblends having high mechanical strength, high stiffness, high heat distortion temperatures, low moisture absorption, and good impact strength.

It is a further object of the invention to improve the impact properties of blends of polyamides and styrene/unsaturated carboxylic acid copolymers while maintaining a high degree of resistance to oxidative degradation.

According to this invention, there is provided a moldable thermoplastic polymer blend comprising: (A) from about 9 to 94 weight percent of a polyamide having a number average molecular weight of at least about 8,000; (B) from about 5 to 90 weight percent of a thermoplastic copolymer of an α,β -unsaturated carboxylic acid, a monovinyl aromatic monomer, and optionally, an unsaturated monomer selected from the group consisting of unsaturated carboxylic acid imides, unsaturated carboxylic acid esters, and unsaturated nitriles, said thermoplastic copolymer having a number average molecular weight of at least about 30,000; and (C) from about 1 to 30 weight percent of a functionalized elastomer comprising an adduct of an α,β -unsaturated carboxylic acid anhydride and an elastomeric polymer selected from the group consisting of: (a) a random copolymer of ethylene, at least one C_3 to C_6 α -olefin, and at least one diene; (b) a block copolymer wherein at least two blocks consist essentially of recurring units of at least one monovinyl aromatic monomer and at least one other block consists essentially of recurring units of at least one conjugated diene, and wherein said other block is substantially hydrogenated such that the unsaturation level of said other block is less than 20 percent of the original unsaturation level; (c) a substantially random copolymer of at least one monovinyl aromatic monomer and at least one conjugated diene, wherein said random copolymer is substantially hydrogenated such that the unsaturation level of said random copolymer is less than 20 percent of the original unsaturation level; and (d) a polymer of at least one conjugated diene, wherein said polymer is substantially hydrogenated such that the unsaturation level of said polymer is less than 20 percent of the original unsaturation level.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The moldable multi-phase polyblends of this invention are tough rigid thermoplastics having a fine dispersion microstructure observable by electron microscopy. The compositions of the continuous and disperse phases depend on the relative amounts of the blend components employed. The disperse phase when viewed by electron microscopy appears as particles of extremely small average diameter. It is preferred that the average diameter of the particles be as small as possible, with the preferred diameter being less than about 5 microns. Most preferably, the particle diameter is less than about 2 microns. The particle size of the disperse phase is much smaller than would be expected from the large difference in the solubility parameters of the individual components of the polyblend.

Without wishing to be bound by any particular theory, it is believed that partial miscibility or compatibilization of the polyamide and thermoplastic copolymer, resulting in the excellent overall balance of properties possessed by the polyblends, is achieved by chemical reaction of the amine end-groups of the polyamide with the acid functionality of the thermoplastic copolymer. The polyamide may undergo limited degradation and chain scission during blending to create additional amine groups available for reaction with the acid functionality. The chemical reaction is thought to yield a graft copolymer in which polyamide segments appear as side-chains on a backbone of thermoplastic copolymer.

The superior impact properties of the polyblends of this invention, as compared to blends of polyamides and styrene/unsaturated carboxylic acid copolymers alone, are believed to be due to chemical reaction of the amine groups of the polyamide with the carboxylic acid anhydride groups of the functionalized elastomer. The compatibilization which results from this grafting helps to ensure that the elastomeric polymer is well-dispersed throughout the polyblend matrix and is at least partially compatibilized with the matrix, thereby functioning effectively as an impact modifier.

However, the polyblends of this invention can include not only the graft copolymers described above, but also varying amounts of ungrafted polyamide, ungrafted functionalized elastomer, and ungrafted thermoplastic copolymer. The relative amounts of the graft copolymer, unreacted polyamide resin, and unreacted thermoplastic copolymer will depend on the component molecular weights, the chemical composition of the components, and blending temperature and shear rate, among other factors. In general, however, it is desirable to achieve a high proportion of the graft copolymer in the blend.

The polyamide resin may constitute from about 9 to 94 weight percent, more preferably from about 40 to 70 weight percent, of the total polyblend of this invention. Any polyamide is suitable for use in the practice of this invention, provided it has a number average molecular weight of at least about 8,000. Aliphatic polyamides are preferred. It is preferred that the polyamide have an average of at least 0.5 amine end-group per chain. The preferred molecular weight range is from about 10,000 to 40,000. Suitable polyamides include nylon-6, nylon-6,6, nylon-6,9, nylon-6,10, nylon-6,12, nylon-11, nylon-12 and mixtures thereof. Nylon-6 (polycaprolactam) is a preferred polyamide resin. The polyamide resins may

be prepared by any of the methods familiar to those skilled in the art, including the condensation of diamines and diacid chlorides, the condensation of diamines and dicarboxylic acids, and the ring-opening polymerization of lactams.

The polyblends of this invention are comprised of from about 5 to 90 weight percent, preferably about 15 to 45 weight percent, of a thermoplastic copolymer. The thermoplastic copolymer preferably contains from about 1 to 30 weight percent of an unsaturated carboxylic acid, from about 50 to 99 weight percent of a vinyl aromatic monomer, and, optionally, up to about 40 weight percent of an unsaturated monomer. The unsaturated monomer is selected from the group consisting of unsaturated dicarboxylic acid imides, unsaturated nitrile monomers, and unsaturated carboxylic acid esters. The unsaturated carboxylic acid is most preferably incorporated in a random fashion into the thermoplastic copolymer.

The unsaturated carboxylic acids suitable for incorporation into the thermoplastic copolymer component of this invention are preferably C_3 - C_8 α,β -unsaturated aliphatic monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, 2-pentenoic acid, angelic and tiglic acid. Unsaturated dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid, and citraconic acid may also be used, either alone or in combination with unsaturated monocarboxylic acids. Methacrylic acid is the preferred unsaturated carboxylic acid. It is preferred that the thermoplastic copolymer contain from about 1 to 15 weight percent of the unsaturated carboxylic acid as optimum properties, particularly impact strength, are obtained at these relatively low levels of acid. The presence of greater amounts of acid tends to result in cross-linking, lower mechanical strength, and poorer impact properties, although this can be partially compensated for by carrying out the blending under conditions such that a lower degree of chemical reaction and grafting takes place between the polyamide and the thermoplastic copolymer.

The thermoplastic copolymer is additionally comprised of at least one vinyl aromatic monomer copolymerizable with the unsaturated carboxylic acid. Suitable vinyl aromatic monomers include such as styrene, α -methylstyrene, ethylstyrene, isopropylstyrene, tert-butylstyrene, vinyl naphthalene, and their mixtures. Styrene is the preferred vinyl aromatic monomer. Unsaturated nitriles such as acrylonitrile and methacrylonitrile, unsaturated carboxylic acid esters, especially C_1 - C_6 alkyl esters of acrylic acid and methacrylic acid such as methyl methacrylate and n-butyl acrylate, may also be used in addition to the vinyl aromatic monomer. Unsaturated dicarboxylic acid imide derivatives such as n-phenylmaleimide and maleimide are also useful as comonomers. In contrast to the unsaturated carboxylic acid repeating units, the imide derivatives do not appear to chemically react with the polyamide resin component when incorporated into the thermoplastic polymer blends of this invention. Good compatibilization, small disperse particle size, and good impact properties are not achieved if the thermoplastic copolymer contains imide but not acid. However, the presence of imide together with acid can improve certain properties of the final polyblend, such as stiffness and heat distortion temperature.

The preferred thermoplastic copolymers of this invention are styrene/methacrylic acid copolymers con-

taining from about 1 to 15 weight percent acid. Particularly suitable for use are the high molecular weight copolymers of styrene and methacrylic acid designated as "Ryulex" copolymers, commercially available from Dainippon Ink and Chemicals Company.

The thermoplastic copolymers may be prepared by any of the several methods available for their synthesis. For example, the copolymers may be obtained by solution copolymerization directly from the respective monomers as described in U.S. Pat. Nos. 3,035,033, 4,275,182, 2,967,855, and 4,195,169, Jpn. Kokai No. 62-95-305, and EP Appl. 333,440. Alternatively, a suspension polymerization process as taught in U.S. Pat. Nos. 4,656,112, 4,631,307 and 3,839,308 and Jpn. Kokai No. 60-168,709 may be employed. The teachings of all these patents are incorporated herein by reference. The number average molecular weight of the thermoplastic copolymer is at least about 30,000, and preferably is less than about 500,000.

The thermoplastic copolymer can be impact-modified using any art-recognized method of incorporating one or more rubber impact modifiers. Typically, such impact modifiers are polymers which are elastomeric in nature and which have glass transition temperatures below 0° C. (preferably, below -30° C.). Examples of suitable impact modifiers include butadiene rubber, ethylene-propylene-diene monomer (EPDM) rubber, butadiene-acrylonitrile rubber, butadiene-styrene rubber, isoprene rubber, isoprene-styrene rubber, and block copolymers of butadiene-styrene. Preferably, the impact modifiers are incorporated into the thermoplastic copolymer monomer mixture prior to polymerization in order to chemically graft the impact modifier onto the thermoplastic copolymer. The methods described in U.S. Pat. Nos. 3,657,395, and 4,631,307 and Jpn. Kokai No. 62-95,305 (incorporated herein by reference) are exemplary.

The use of thermoplastic copolymer which is impact-modified is optional, as the impact properties of the polyblends of this invention are influenced more by the amount and type of functionalized elastomer used. It is preferred that the thermoplastic copolymer contain between about 2 and 25 parts by weight rubber per 100 parts thermoplastic copolymer if it is rubber-modified.

The functionalized elastomer may constitute from about 1 to 30 weight percent of the total polyblend of the invention, with 10 to 20 weight percent being the preferred range. The functionalized elastomers suitable for use in the moldable polyblends of this invention are relatively soft, rubber-like polymers containing at least one pendent carboxylic acid anhydride group per polymer chain which provides a potential grafting site for reaction with a polyamide amine end-group. The anhydride group is preferably pendent and not incorporated as a monomer unit in the backbone of the elastomeric polymer. To function effectively as an elastomer, this component should have a glass transition temperature less than 0° C.; more preferably, the glass transition temperature should be less than -40° C. The molecular weight of the functionalized elastomer should be sufficiently high so as to provide adequate elastomeric properties. In most instances, the number average molecular weight will preferably be above about 30,000. The functionalized elastomers should contain a minimum of cross-linking or gel in order to facilitate processing of the polyblends of this invention. Some degree of branching may be desirable, however.

A particular advantage of this invention is that the functionalized elastomers used contain relatively low levels of unsaturation, as compared to, for example, elastomers containing substantial amounts of butadiene. The presence of low levels of unsaturation results in the polyblends of this invention having excellent weather resistance, particularly with respect to oxidation.

The α,β -unsaturated carboxylic acid anhydrides suitable for use in preparing the adducts to be used in the polyblends of this invention are those anhydrides which may be grafted onto the random copolymer to provide amine-reactive functional groups. A particularly preferred anhydride is maleic anhydride, although other anhydrides such as citraconic anhydride, itaconic anhydride, tetrahydrophthalic anhydride, chloromaleic anhydride, and ethyl maleic anhydride may also be employed. It is desirable that the anhydride constitute from about 0.5 to 5 weight percent of the adduct.

In one embodiment, the functionalized elastomer may be an adduct of an α,β -unsaturated carboxylic acid anhydride and a random copolymer of ethylene, at least one C₃ to C₆ α -olefin, and at least one diene. This type of random terpolymer is the type generally referred to in the art as "EPDM" rubber. The α -olefin is preferably propylene, for reasons of availability, but may also be 1-butene, 1-pentene, 1-hexene or mixtures thereof. The diene suitable for use in preparing the random copolymer can be a conjugated diene such as 1,3-butadiene or isoprene, but more preferably may be a nonconjugated diene. The nonconjugated diene may be a linear aliphatic diene of at least six carbon atoms which has either two terminal double bonds or one terminal double bond and one internal double bond. Alternatively, the nonconjugated diene may be a cyclic diene wherein one or both of the double bonds are part of a carboxycyclic ring. The structure of the copolymer may be altered as desired, particularly with respect to branching, by the selection of particular nonconjugated dienes as is well known to those skilled in the art. Particularly preferred nonconjugated dienes include 1,4-hexadiene, dicyclopentadiene, and 5-ethylidene-2-norbornene.

In this embodiment, it is preferred that the random copolymer contain from about 40 to 90 mole percent ethylene and 0.1 to 7.5 mole percent diene, with the remainder being propylene.

The adducts of α,β -unsaturated carboxylic acid anhydrides and random copolymers of ethylene, at least one C₃ to C₆ α -olefin, and at least one diene which are suitable for use in the polyblends of this invention may be prepared by any of the methods well-known to those skilled in the art. U.S. Pat. Nos. 3,884,882 and 4,010,223, and European Pat. Appl. No. 353,720 incorporated herein by reference, teach the preparation of such adducts by thermally reacting maleic anhydride and EPDM type rubbers. Examples of suitable functionalized elastomers of this type are Uniroyal "ROYALTUF 465" and Uniroyal "ROYALTUF 465A", which are maleated-EPDM rubbers containing about 1.2 and 0.7 weight percent maleic anhydride respectively.

In another embodiment, the functionalized elastomer is an adduct of an α,β -unsaturated carboxylic acid anhydride and a hydrogenated block copolymer wherein at least two blocks consist essentially of recurring units of at least one monovinyl aromatic monomer and at least one other block consists essentially of recurring units of a conjugated diene. The monovinyl aromatic monomer is most preferably styrene, but may be any other similar monomer such as α -methylstyrene, p-methylstyrene,

p-ethylstyrene, p-tert-butyl styrene or p-chlorostyrene. Suitable conjugated dienes include butadiene and isoprene.

The 1,2-microstructure content of the conjugated diene block may be from about 7 to 100%. The block copolymer may contain up to 60 percent by weight of monovinyl aromatic monomer; higher monovinyl aromatic monomer content may yield block copolymers which are not sufficiently elastomeric.

The block copolymer is hydrogenated in order to reduce the level of unsaturation due to the conjugated diene block to less than 20 percent of the original value before hydrogenation. As discussed previously, the low levels of unsaturation provide the final polyblend with a high degree of resistance toward oxidative degradation.

The blocks of recurring monovinyl aromatic monomer units constitute relatively hard segments having a glass transition temperature or melting temperature above ambient while the block of conjugated diene is a relatively soft rubbery segment having a glass transition temperature below ambient. The block copolymer is thus a thermoplastic elastomer.

The adducts of α,β -unsaturated carboxylic acid anhydrides and hydrogenated block copolymers of monovinyl aromatic compounds and conjugated dienes suitable for use as functionalized elastomers in the polyblends of this invention may be prepared by any of the methods known in the art. U.S. Pat. No. 4,427,828, incorporated herein by reference, teaches the preparation of such adducts by thermally grafting the anhydride onto the hydrogenated block copolymer using an "ene"-type reaction. U.S. Pat. No. 4,578,429, incorporated herein by reference, teaches that similar adducts may also be obtained by free radical induced grafting. In this method, the resulting adducts are more thermally stable than the adducts of U.S. Pat. No. 4,427,828 due to the type of grafting which occurs. In addition, the functionalized hydrogenated block copolymers produced by free radical grafting may contain even lower levels of unsaturation since the presence of double bonds in the block copolymer is not required by this type of grafting mechanism. "Kraton FG1901X", a maleated block copolymer sold commercially by Shell which contains ca. 2 wt. % maleic anhydride, is an example of a suitable functionalized elastomer of this type. Such materials are sometimes referred to as functionalized styrene-ethylene/1-butene-styrene (S-E/B-S) rubbers, as the structure of the butadiene center block after hydrogenation resembles that of an ethylene/1-butene copolymer.

In another embodiment of this invention, the functionalized elastomer is an adduct of an α,β -unsaturated carboxylic acid anhydride and a hydrogenated random copolymer of at least one monovinyl aromatic monomer and at least one conjugated diene. Styrene is the preferred monovinyl aromatic monomer and preferably does not represent more than about 60 mole percent of the random copolymer in order that the glass transition temperature not be increased past the point at which the random copolymer would no longer function effectively as an elastomer. Other monovinyl aromatic monomers may be employed, however, including α -methyl styrene, o- or p-methylstyrene, p-tert-butylstyrene, p-chlorostyrene, vinyl naphthalene, and the like or mixtures thereof. Suitable conjugated dienes include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and similar compounds, with 1,3-butadiene being the preferred diene. The random copolymer is

hydrogenated to lower the unsaturation level to less than 20 percent of the original value. The 1,2-microstructure content of the random copolymers prior to hydrogenation can vary from about 10 to 100 percent. The preparation of adducts of this type is taught in U.S. Pat. No. 4,427,828, which teaches that random copolymers of conjugated dienes and monovinyl aromatic monomers may be functionalized with α,β -unsaturated carboxylic acid anhydrides in a thermal "ene"-type reaction. The teachings of this patent are incorporated herein by reference. Other methods of preparing such adducts will be well-known to those skilled in the art.

In yet another embodiment of this invention, a functionalized elastomer is employed which is an adduct of an α,β -unsaturated carboxylic acid anhydride and a hydrogenated polymer of at least one conjugated diene. The diene polymer is hydrogenated to an extent such that less than 20 percent of the original unsaturation remains. The diene may be any hydrocarbon containing two conjugated double bonds such as 1,3-butadiene, which is the preferred diene. Examples of other suitable dienes include isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and the like. Mixtures of dienes may also be employed. Polymers of conjugated dienes which may be utilized include those containing prior to hydrogenation a total of about 0.1 to 100 percent 1,2- and 3,4-microstructure content and about 0.1 to 99 percent 1,4-microstructure. It is preferred that the 1,2-microstructure content be from about 40 to 60 percent. "Ene"-type thermal grafting may be used to form adducts of this type, as described in U.S. Pat. No. 4,427,828 (incorporated by reference). Other synthetic routes to such adducts will be apparent to those familiar with the art.

The moldable multi-phase polyblends of this invention can be prepared by blending in the melt the polyamide resin, thermoplastic copolymer, and the anhydride functionalized elastomer. It is desirable to carry out such blending under conditions which promote chemical grafting of the polyamide resin onto the thermoplastic copolymer through the acid groups of the copolymer and the anhydride groups of the functionalized elastomer. Intimate and thorough mixing is thus preferred. The melt-blending can be effected using a conventional melt-kneading or compounding apparatus for resins such as a kneader, Banbury mixer, or twin or single screw extruder. The blending may be carried out at a temperature of between 240° C. and 330° C., preferably 260° C. to 310° C. Higher temperatures may result in excessive decomposition, while the desired degree of grafting and compatibilization may not be realized at lower temperatures. It is preferred to carry out the blending under vacuum in order to remove any water formed during reaction of the acid groups in the thermoplastic copolymer and the anhydride groups in the functionalized elastomer.

In a preferred method for the preparation of the moldable thermoplastic polymer blends of this invention, the polyamide and the functionalized elastomer and, optionally, a minor portion of the thermoplastic copolymer are melt-blended to form a first blend composition. The first blend composition is then melt-blended with the remainder of the thermoplastic copolymer to form the final moldable polymer blend. The amount of the first portion of the thermoplastic copolymer is no greater than the amount of the second portion of the thermoplastic copolymer. Preferably, however, the first portion is no greater than about 50 percent by weight of the second portion. For reasons which are not

well understood, this procedure results in significantly improved low temperature impact properties as compared to the properties obtained if all of the components are blended in a single step.

Each step of the blending procedure may be carried out at a temperature of between about 240° C. and 330° C., preferably 260° C. to 310° C. The blending time required in each step will vary depending on the temperature, the blend composition, and the degree of shear present, among other factors, but will typically be from about 10 seconds to 30 minutes.

The polyblends of this invention may be produced by preblending the polyamide and functionalized elastomer (and, optionally, a minor portion of the thermoplastic copolymer). The preblend, which can be in the form of pellets, for example, is then melt-blended with the remaining components of the thermoplastic resin composition. The process of this invention may also be conveniently carried out using a single pass through an extruder. The polyamide and the functionalized elastomer (and the first portion of the thermoplastic copolymer, if any) are fed into the extruder at a first feed port and melt-blended before introduction of the thermoplastic copolymer at one or more downstream feed ports. The total residence time in the extruder will generally be from about 0.5 to 10 minutes.

In another preferred embodiment of the process of this invention, the polyamide is first melted and then melt-blended with the other components of the thermoplastic resin composition (the functionalized elastomer and the thermoplastic copolymer). This procedure may most conveniently be carried out using an extruder equipped with multiple feed ports. The polyamide is added through the first feed port; the other components are then introduced at one or more downstream feed ports to the molten polyamide. Processing temperatures are preferably from about 240° C. to 330° C. (more preferably, from about 260° C. to 310° C.).

The multi-phase polyblends of this invention may additionally include additives such as heat or light stabilizers, anti-oxidants, pigments, anti-static agents or fillers such as glass or carbon fibers. The polyblends may be employed in any application for which thermoplastic resins are normally used, including extrusion, injection or blow molding.

The following examples are meant to illustrate, but not limit, the invention. The evaluation of material properties was performed based on the following ASTM standard tests: flexural strength and modulus (D-790), tensile strength (D-638), notched Izod (D-256), DTUL (deflection temperature under load at 264 psi, D-648), and penetration impact (D-3763).

EXAMPLES 1-5

These examples demonstrate the preparation of the moldable thermoplastic polymer blends of this invention. The following blend methods and components were employed.

- Blend Method M-1: The polyamide, functionalized elastomer and thermoplastic copolymer were extruded in a two stage, single screw Egan extruder in a single pass.
- Blend Method M-2: The polyamide and functionalized elastomer were melt-blended using a Welding Engineers counter-rotating non-intermeshing twin screw devolatilizing extruder. The thermoplastic copolymer was then added to the molten

-continued

Blend Method M-3:	polyamide/functionalized elastomer mixture at a downstream feed port. The polyamide and functionalized elastomer were melt-blended and pelletized using a ZSK extruder. The pelletized mixture was then melt-blended with the thermoplastic copolymer using a Welding Engineers counter-rotating non-intermeshing twin screw devolatilizing extruder.	
<u>Polyamides</u>		
A-1:	"Nivionplast 273 MR", a nylon-6 polyamide available from Enichem.	
A-2:	"Nivionplast 303 HV", a nylon-6 polyamide having a number average molecular weight of 28,000 and containing 0.041 meq NH ₂ /gram, available from Enichem.	
<u>Functionalized Elastomer</u>		
B-1:	"Royaltuf 465", a maleated-EPDM rubber containing about 1.2 weight percent grafted maleic anhydride; available from Uniroyal.	
<u>Thermoplastic Copolymers</u>		
C-1:	A styrene/methacrylic acid copolymer containing about 7 weight percent methacrylic acid prepared in powder form by suspension polymerization.	
C-2:	"Ryulex A-11" styrenic/methacrylic acid copolymer estimated to contain about 10 weight percent methacrylic acid, available from Dainippon Ink and Chemicals Co.	

TABLE I

EXAMPLE NO.	1	2	3	4	5
Polyamide	A-1	A-1	A-2	A-2	A-2
pbw	56	56	56	56	56
Functionalized Elastomer	B-1	B-1	B-1	B-1	B-1
pbw	14	14	14	14	14
Thermoplastic Copolymer	C-1	C-2	C-1	C-2	C-2
pbw	30	30	30	30	30
Blending Method	M-1	M-2	M-1	M-2	M-3
Tensile					
Yield Stress (ksi)	8.2	8.1	8.2	8.5	8.9
Break Strain (%)	20	30	22	21	30
Flex					
Modulus (ksi)	330	315	370	357	360
Yield Stress (ksi)	13.7	12.7	15.2	13.9	14.6
DTUL (°F.)					
Instrument Impact					
T = 73° C.					
Max. Load (lb)	1110	1016	788	1013	1070
Total Energy (ft-lb)	53	42	10	43	45
T = -20° F.					
Max. Load (lb)	227	1260	332	1197	1026
Total Energy (ft-lb)	2.2	26	2.0	16	18
T = -40° F.					
Max. Load (lb)	—	1297	—	723	660
Total Energy (ft-lb)	—	30	—	7	6
Notched Izod (ft-lb/in)					

TABLE I-continued

EXAMPLE NO.	1	2	3	4	5
T = 73° F.	1.8	6.6	1.4	4.1	7.5
T = -20° F.	1.7	2.2	0.99	2.4	2.6
T = -40° F.	—	2.0	—	2.1	2.4

EXAMPLES 6-9

The preparation of moldable thermoplastic polymer blends containing various polyamides, functionalized elastomers, and thermoplastic copolymers in varying proportions is illustrated by these examples. The following blend methods and components are employed.

Blend Methods See Examples 1-5

M-1,

M-2,

M-3:

Blend Method

M-4:

The procedure described above for Blend Method M-2 is followed, except that 10 parts by weight thermoplastic copolymer is initially blended with the polyamide and functionalized elastomer. The remaining thermoplastic copolymer (28 parts by weight) is then added through a downstream feed port.

A-3: "Zytel 151 LNC-10" polyamide, a nylon-6,12 available from E. I. duPont de Nemours.

A-4: "Vestamid L 1901" polyamide, a nylon-12 available from Huls America.

A-5: "BMNO P40" polyamide, a nylon-11 available from Atochem.

A-6: "Zytel 101" polyamide, a nylon-6,6 available from E. I. duPont de Nemours.

Functionalized Elastomers

B-2: Shell Chemical "Kraton FG 1901X" maleic anhydride functionalized hydrogenated styrene/butadiene block copolymer containing 2 weight percent maleic anhydride and 28 weight percent polymeric styrene.

B-3: Hydrogenated styrene/butadiene block copolymer containing about 0.5 weight percent grafted maleic anhydride and 29 weight percent polymeric styrene and having a molecular weight of about 54,000; prepared in accordance with Examples 1-5 of U.S. Pat. No. 4,795,782.

B-4: Maleic anhydride functionalized EPHD rubber prepared in accordance with Example 1 of U.S. Pat. No. 3,884,882; maleic anhydride content about 2 weight percent; inherent viscosity about 1.5; monomer composition of EPHD rubber, 61.4 weight percent ethylene, 32 weight percent ethylene, and 6.6 weight percent 1,4-hexadiene.

B-5: Hydrogenated maleic anhydride functionalized, polybutadiene prepared in accordance with Example 1 of U.S. Pat. No. 4,427,828; M_w 170,000; maleic anhydride content about 5 weight percent.

Thermoplastic Copolymers

C-3: A styrene/ethyl acrylate/acrylic acid terpolymer containing 58.3 weight percent styrene, 35 weight percent ethyl acrylate, and 6.7 weight percent acrylic acid, prepared in accordance with Example 3 of U.S. Pat. No. 2,967,855.

C-4: A styrene/methacrylic acid copolymer containing 5.6 weight percent methacrylic acid, prepared in accordance with Example 8 of U.S. Pat. No. 4,195,196.

C-5: A styrene/methyl methacrylate/methacrylic acid terpolymer containing 48 weight percent styrene, 35 weight percent methyl methacrylate, and 17 weight percent methacrylic acid and 6 parts by weight per 100 parts by weight terpolymer of a styrene-butadiene rubber (30% styrene), prepared in accordance with Example 6 of Jpn. Pat. No. 62-95-305.

C-6: A styrene/methacrylic acid copolymer containing 89 weight percent styrene and 11 weight percent

-continued

methacrylic acid and 8.7 parts by weight per 100 parts by weight copolymer of a polybutadiene rubber, prepared in accordance with Example 3 of U.S. Pat. No. 4,631,307.

TABLE II

EXAMPLE NO.	6	7	8	9
10 Polyamide	A-3	A-4	A-5	A-6
pbw	70	45	65	50
Functionalized Elastomer	B-2	B-3	B-4	B-5
pbw	10	10	15	18
Thermoplastic Copolymer	C-3	C-4	C-5	C-6
pbw	15	45	20	32
15 Blending Method	M-3	M-4	M-2	M-3

I claim:

1. A process for producing a moldable thermoplastic polymer blend having enhanced low temperature impact properties comprising the steps of:

(A) forming a first blend composition by melt-blending at a temperature of from 240° C. to 330° C. and for a time of from 10 seconds to 30 minutes

(i) a polyamide having a number average molecular weight of at least about 8,000;

(ii) a functionalized elastomer which is an adduct of an α , β -unsaturated carboxylic acid anhydride and an elastomeric polymer selected from the group consisting of:

(a) a random copolymer of ethylene, at least one C_3 to C_6 α -olefin, and at least one nonconjugated diene,

(b) a block copolymer wherein at least two blocks consist essentially of recurring units of at least one monovinyl aromatic monomer and at least one other block consists essentially of recurring units of at least one conjugated diene, and wherein said other block is substantially hydrogenated such that the unsaturation level of said other block is less than 20 percent of the original unsaturation level;

(c) a random copolymer of at least one monovinyl aromatic monomer and at least one conjugated diene, wherein said random copolymer is substantially hydrogenated such that the unsaturation level of said random copolymer is less than 20 percent of the original unsaturation level; and

(d) a conjugated diene polymer, wherein said conjugated diene polymer consists of a conjugated diene or a mixture of conjugated dienes and is substantially hydrogenated such that the unsaturation level of said polymer is less than 20 percent of the original unsaturation level; and

(iii) optionally, a first portion of a thermoplastic copolymer comprised of from about 1 to 30 weight percent based on thermoplastic copolymer of an α , β -unsaturated carboxylic acid, from about 50 to 99 weight percent based on thermoplastic copolymer of a monovinyl aromatic monomer, and up to about 40 weight percent of an unsaturated monomer selected from the group consisting of unsaturated dicarboxylic acid imides, unsaturated nitrile monomers, and unsaturated carboxylic acid esters, said thermoplastic copolymer having a number average molecular

weight of at least about 30,000 wherein said melt-blending is carried out under conditions effective to promote chemical grafting of the polyamide and the functionalized elastomer; and

- (B) melt-blending said first blend composition and a second portion of the thermoplastic copolymer under vacuum with removal of water at a temperature of from 240° C. to 330° C. and for a time of from 10 seconds to 30 minutes, with the proviso that the amount of the first portion of the thermoplastic copolymer is no greater than the amount of the second portion of the thermoplastic copolymer, wherein said melt-blending is carried out under conditions effective to promote chemical grafting of the polyamide and the thermoplastic copolymer.

2. The process of claim 1 wherein the resulting moldable polymer blend is comprised of from about 9 to 94 weight percent of the polyamide, from about 5 to 90 weight percent of the thermoplastic copolymer, and from about 1 to 30 weight percent of the functionalized elastomer.

3. The process of claim 1 wherein the polyamide is selected from the group consisting of nylon-6, nylon-6,6, nylon-6,12, nylon-6,10, nylon-11, and nylon-12.

4. The process of claim 1 wherein the α,β -unsaturated carboxylic acid in the thermoplastic copolymer is selected from the group consisting of acrylic acid and methacrylic acid.

5. The process of claim 1 wherein the vinyl aromatic monomer in the thermoplastic copolymer is styrene.

6. The process of claim 1 wherein the thermoplastic copolymer is a styrene/methacrylic acid copolymer.

7. The process of claim 1 wherein melt-blending steps (A) and (B) are performed at a temperature of from about 260° C. to 310° C.

8. A process for producing a moldable polymer blend having enhanced low temperature impact properties comprising the steps of:

- (A) forming a first blend composition by melt-blending at a temperature of from about 240° C. to 330° C. and for a time of from 10 seconds to 30 minutes:
- (i) nylon-6 having a number average molecular weight of at least about 8,000;
 - (ii) a functionalized elastomer which is an adduct of maleic anhydride and an elastomeric polymer selected from the group consisting of:

(a) a random copolymer of ethylene, propylene, and at least one nonconjugated diene selected from the group consisting of 1,4-hexadiene, 5-ethylidene-2-norbornene, and dicyclopentadiene

(b) a block copolymer wherein at least two blocks consist essentially of recurring units of styrene and at least one other block consists essentially of recurring units of butadiene, and wherein said other block is substantially hydrogenated such that the unsaturation level of said other block is less than 20 percent of the original unsaturation level;

(c) a random copolymer of styrene and butadiene, wherein said random copolymer is substantially hydrogenated such that the unsaturation level of said random copolymer is less than 20 percent of the original unsaturation level; and

(d) a polymer of butadiene, wherein said polymer consists of butadiene and is substantially hydrogenated such that the unsaturation level of said polymer is less than 20 percent of the original unsaturation level wherein said melt-blending is carried out under conditions effective to promote chemical grafting of the nylon-6 and the functionalized elastomer; and

(B) melt-blending under vacuum with removal of water for a time of from 10 seconds to 30 minutes at a temperature of from about 240° C. to 330° C. said first blend composition and a thermoplastic copolymer of from about 70 to 99 weight percent styrene and from about 1 to 30 weight percent of an unsaturated carboxylic acid selected from the group consisting of methacrylic acid and acrylic acid and having a number average molecular weight of at least about 30,000, wherein said melt-blending is carried out under conditions effective to promote chemical grafting of the nylon-6 and the thermoplastic copolymer;

and wherein the resulting moldable polymer blend contains from about 40 to 70 weight percent of the nylon-6, from about 15 to 45 weight percent of the thermoplastic copolymer, and from about 10 to 20 weight percent of the functionalized elastomer and step (A) is performed in the absence of any of the thermoplastic copolymer.

* * * * *

EXHIBIT I

Industrial Chemistry Library, Volume 4

Technology of Corn Wet Milling

and Associated Processes

by

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Chapter 4

CORN STARCH: PROPERTIES

4.1 BIOSYNTHESIS

4.1.1 Occurrence

Starch, in the form of minute granules, is the major constituent of corn and is found in many other plants. Its exact composition, and the size and shape of the granules, depends upon the plant source (Table 4.1).

The presence of starch in large quantities in plant seeds, such as the corn kernel, provides a food reserve to permit growth to become established in the first few days after germination, at which time the newly developing roots are not yet effective. Such crops form high energy constituents of human foods and animal feed, and, when the starch can be separated easily in a relatively pure form, they provide a source of derived products for food and industrial use.

4.1.2 Granule formation

Corn starch is formed in small bodies, the plastids or amyloplasts, which are part of the cells of the kernel endosperm. Enzyme systems in the amyloplasts are responsible for assembling basic materials into the complicated macromolecules of which the starch granule is composed. At an early stage of development there may be more than one embryo starch granule in each amyloplast, but as they grow, they subdivide in such a way that each daughter amyloplast contains only one granule.

Starch is a polyglucan, which is a polymer formed almost entirely of chains of anhydro-glucose units. The chains are of two basic types, amylose being linear and amylopectin branched, and it seems likely that the synthesis of each component is directed by a separate enzyme system.

The amylose and amylopectin macromolecules are arranged more or less radially in the granule in a semi-crystalline form established by hydrogen bonding (Section 4.3.1), the main structural element being amylopectin. Growth of the granule is effected by

TABLE 4.1
PROPERTIES OF STARCHES

TYPE OF STARCH	CORN (MAIZE)	WAXY MAIZE	AMYLOMAIZE HIGH AMYLOSE
Granule size in microns	Average 15 Smallest 5 Largest 25	Average 15 Smallest 5 Largest 25	Average 10 Smallest 2 Largest 24
Granule shape	Round, polygonal	Round polygonal (as-corn)	Round elongated, multiple
Pattern under polarized light	Black cross	Black cross	Black cross, but frequently absent
Approx. amylose/ amylopectin	26/74	1/99	Up to 80/20
Gelatinization temp. range $^{\circ}\text{C}$ $^{\circ}\text{F}$	62/72 144/162	63/72 145/162	67/100+ 153/212+
Total lipid content approx %	0.5	0.3	0.4
Paste clarity	Opaque	Translucent	Opaque*
Paste texture	Short, heavy body	Long, stringy fluid body	Hard gel*
Paste strength under mechanical shear & prolonged heat	Medium	Low	Medium*
Paste viscosity	Medium, pronounced set-back	Medium/high, no irreversible set-back	Medium/low, very pronounced set-back*
Taste & Odor	Low	Low	Low

*High amylose starch will not disperse properly unless pressure-cooked to 150°C (302°F).

TABLE 4.1
PROPERTIES OF STARCHES

TYPE OF STARCH	WHEAT	POTATO	SWEET POTATO
Granule size in microns	Two fractions 2-10 20-35	Variable 15-100	Average 15 Smallest 10 var. Largest 25
Granule shape	Round, elliptical	Egg-like with striations like oyster shell	Polygonal
Pattern under polarized light	Black cross	Irregular black cross	Black cross
Approx. amylose/ amylopectin content	25/75	24/76	18/82
Gelatinization temp. range $^{\circ}\text{C}$ $^{\circ}\text{F}$	52/64 126/147	56/69 133/156	58/74 136/165
Total lipid content approx. %	1.0	Very low	Very low
Paste clarity	Opaque	Translucent	Translucent
Paste texture	Short, heavy	Long, stringy fluid body	Long, stringy fluid body
Paste strength under mechanical shear & prolonged heat	Medium	Low	Low
Paste viscosity	Med/low, pronounced set-back	Very high moderate set-back	High, moderate set-back
Taste and odor	Low	Slight cucumber- like	Low

TABLE 4.1
PROPERTIES OF STARCHES

TYPE OF STARCH	RICE	GRAIN SORGHUM	WAXY SORGHUM
Granule size in microns	Variable 3-8	Average 15 Smallest 5 Largest 25	Average 15 Smallest 6 Largest 30
Granule shape	Polygonal, occurring in clusters	Round, polygonal (as corn)	Round polygonal (as corn)
Pattern under polarized light	Indistinct because of small size	Black cross	Black cross
Approx. amylose/amylopectin content	17/83	26/74	1/99
Gelatinization temp. range °C °F	61/78 142/172	68/75 154/167	67/74 153/165
Total lipid content approx. %	0.4	0.4	0.3
Paste clarify	Opaque	Opaque	Translucent
Paste texture	Short, heavy body	Short, heavy body	Long, stringy fluid body
Paste strength under mechanical shear & prolonged heat	Medium	Medium	Low
Paste viscosity	Medium/low, pronounced set-back	Medium pronounced set-back	Medium/high, no irreversible set-back
Taste and Odor	Low	Low	Low

TABLE 4.1
PROPERTIES OF STARCHES

TYPE OF STARCH	SAGO	CASSAVA (TAPIOCA)
Granule size in microns	Variable 20-60	Average 20 Smallest 5 Largest 35
Granule shape	Egg-like with some truncated forms	Round, oval indentations
Patter under polarized light	Irregular Black cross	Black cross
Approx. amylose/ amylopectin	27/73	17/83
Gelatinization temp. range ^{°C} ^{°F}	60/72 140/162	52/64 126/147
Total lipid content approx. %	Very low	0.1
Paste clarity	Translucent	Translucent
Paste texture	Long, stringy fluid body	Long, stringy fluid body
Paste strength under mechanical shear & prolonged heat	Med/low	Low
Paste viscosity	Medium/high, moderate set-back	High, low set back
Taste & Odor	Low	Fruity

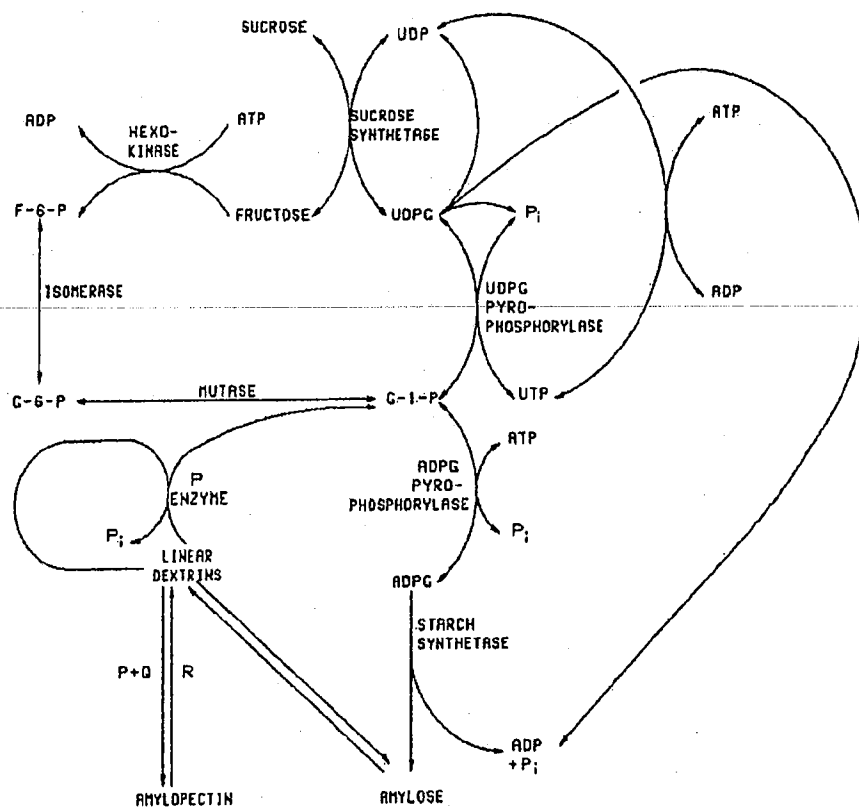


FIGURE 4.1

PROPOSED PATHWAY FOR STARCH SYNTHESIS

FOR KEY SEE TABLE 4.2

TABLE 4.2
ENZYMES PROBABLY INVOLVED IN STARCH SYNTHESIS

NAME	REACTION CATALYZED	REMARKS
Sucrose synthetase	Sucrose + UDP \longrightarrow UDPG + Fructose	
Hexokinase	Fructose + ATP \longrightarrow F-6-P + ADP	
Isomerase	F-6-P \longrightarrow G-6-P	
Mutase	G-6-P \longrightarrow G-1-P	
UDPG pyrophosphorylase	UDPG + P _i \longrightarrow G-1-P + UTP	
ADPG pyrophosphorylase	ADPG + P _i \longrightarrow G-1-P + ATP	
Phosphorylase (P enzyme)	G-1-P + G _n \longrightarrow G _{n+1} + P _i	Forms a linear glucan with alpha 1:4 linkage
O enzyme	Amylose \longrightarrow Amylopectin	
Starch synthetase	ADPG + G _n \longrightarrow G _{n+1} + ADP + P _i UDPG + G _n \longrightarrow G _{n+1} + UDP + P _i	
R enzyme	Amylopectin \longrightarrow Linear dextrans	A debranching enzyme
D enzyme	2G ₃ \longrightarrow G ₅ + G 2G ₄ \longrightarrow G ₇ + G etc., up to about G ₅₀	Also called a disproportionating enzyme

KEY TO ABBREVIATIONS:

UDP	Uridine diphosphate
UTP	Uridine triphosphate
ADP	Adenosine diphosphate
ATP	Adenosine triphosphate

F-6-P	Fructose-6-phosphate
G-6-P	Glucose-6-phosphate
G-1-P	Glucose-1-phosphate

UDPG	Uridine diphosphate glucose
ADPG	Adenosine diphosphate glucose

G _n	A glucose polymer with n anhydro-glucose units
P _i	Inorganic phosphate

deposition of layer upon layer, starting from the "hilum", or botanical center of the granules, which can usually be discerned microscopically. Some variation in the properties of the starch in a granule, particularly an increase in the content of amylose, has been observed to occur as the plant approaches maturity and the granule reaches full size.

There is no evidence for the existence of a membrane surrounding the granule, although in dried starch the outer layers of a granule can acquire a denser structure than the inner, due to the loss of more water.

4.1.3 Enzyme reactions in synthesis

Details of the enzymic reactions involved in the synthesis of starch are still the subject of research, and only a brief outline of current ideas can be given here.

It is envisaged that there are three parts to the system:

- i. Formation of active "primer" molecules
- ii. Building the linear molecular chains by using the primers
- iii. Introduction of branches on the chains.

It is thought that the common starch-degrading enzymes (the various types of "amylases") play little if any part in synthesis, since the reaction equilibria favor breakdown. Raw material for starch synthesis is provided by photosynthesis in the form of glucose phosphates and other low molecular weight materials, but is conveyed about the plant mostly in the form of sucrose. Any scheme to describe the process of starch synthesis must therefore commence with the breakdown of sucrose. Figure 4.1 shows one such scheme, based on the work of Geddes and Greenwood (1), and Table 4.2 lists the major enzymes involved.

If this scheme is followed through it will be seen that the "pool" of linear dextrans provides the "primer" material mentioned above. Once formed, possibly by degradation of amylose, this is built up to amylose by phosphorylase or synthetase, and to amylopectin by phosphorylase plus Q enzyme. It is implied that these enzymes are adsorbed on to the surface of the growing granule, thus imposing a stereochemical control on the polysaccharide structures being deposited.

A number of variations on this hypothesis exist, and more work is required to confirm and clarify the synthetic pathways.

4.2 THE GRANULE

4.2.1 Isolation in the laboratory

The preparation of native starch from laboratory samples of corn presents certain problems. Any dry milling procedure results in a certain amount of damage to the starch granules, and a simulation of the normal wet milling process can reduce the starch viscosity because of inadvertent acid modification in the steeping process.

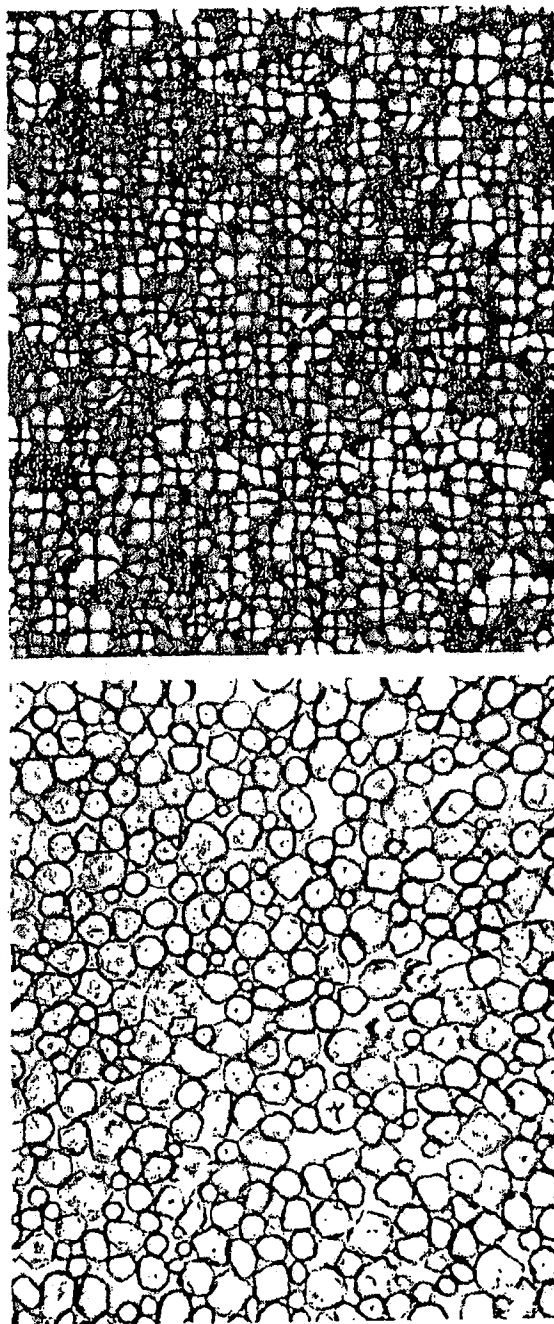
Adkins and Greenwood (2) recommend steeping at 104°F (40°C) for 40-50 hours at pH 6.5 in acetate buffer with .01 M mercuric chloride. This is followed by maceration, slurring in water and successively finer screening to an aperture size of 75 microns. The starch/protein filtrate is then shaken repeatedly with toluene to denature the protein, which may then be separated by light centrifugation.

Where mercuric chloride might be objectionable, Watson (3) indicates that the brief use of steeping fluid which has 0.10% of sulfur dioxide in the form of sodium bisulfite results in no significant degradation of the starch. After steeping for 24 hours at 122°F (50°C) the corn is milled with water in a blender with blunted blades and the slurry passed through successively finer screens to 325 mesh. The starch is finally purified by "tabling" or by repeated centrifuging in the presence of amyl alcohol.

A quantitative recovery of the starch in corn is unlikely to be achieved by these relatively simple procedures. In particular, some of the small granule starch associated with horny endosperm is likely to be lost in the fibrous debris. Watson et al (4) describe a much more elaborate technique for laboratory simulation of the wet milling process, which recovers starch and by-products in approximately the yields and qualities obtained in commercial plant.

4.2.2 Birefringence

When normal starch granules are observed under the microscope using polarized light (crossed Nicol prisms) they appear light against a dark background, typically showing a dark "polarization cross" (Figure 4.2) with its intersection at the hilum. This property of "birefringence", strictly the possession of two refractive indices resulting from the polarization of



REGULAR ILLUMINATION

POLARIZED LIGHT

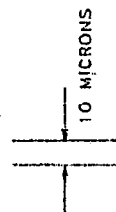


FIGURE 4.2
CORN STARCH GRANULES

(Courtesy of Dr Erik Sorenne, American Malze-Products Co.)

transmitted light, is common in crystalline materials but merely implies that there is some degree of molecular orientation in the granule. The polarization cross is an interference phenomenon due to the spherical shape.

The granules of "waxy" starch, which contain little or no amylose, exhibit normal birefringence, as do granules from which a large part of the amylose has been leached with hot water. The structures responsible must therefore be formed by the amylopectin component. In fact, granules very high in amylose (from amylomaize) often are not birefringent, and have distorted shapes.

The behavior of starch granules in polarized light is sometimes referred to as "anisotropy". This is a more general crystallographic term, but as far as starch granules are concerned it may be assumed to be synonymous with birefringence.

4.2.3 Crystallinity

The molecular detail responsible for crystallinity in a starch granule is not necessarily the same as that conferring birefringence.

Crystallinity is characterized by a fine, regular three-dimensional molecular structure which will produce an x-ray diffraction pattern. Intact starch granules exhibit various types of patterns, depending on the source of starch, moisture level and drying history, and the nature of the responsible structure is not well understood.

In regular corn and waxy maize starch it appears that amylopectin provides the crystalline skeleton, possibly as some type of helical structure. This is a little surprising in view of its branched nature and the difficulty of obtaining crystals in isolated amylopectin.

Amylose, on the other hand, is typically semi-crystalline in isolation. However, only in the case of high amylose starch does amylose appear to play a significant part in the crystallinity of the intact granule.

4.3 CHEMISTRY

4.3.1 Amylose and Amylopectin

As referred to in the earlier sections of this chapter, starch consists of two different types of glucose polymers,

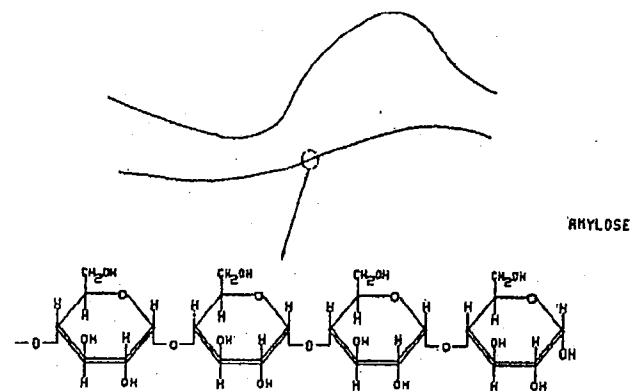
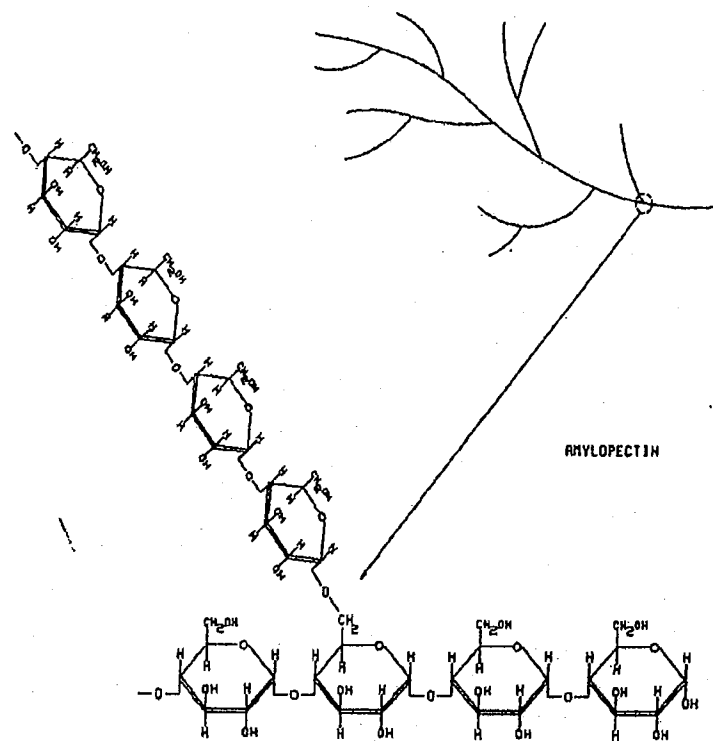


FIGURE 4.3
STARCH COMPONENTS



amylose and amylopectin, with the general formula $(C_6H_{10}O_5)_n$. The predominant linkage between the anhydroglucose units is alpha 1:4, but alpha 1:6 linkages occur in amylopectin, forming branch points as shown in Figure 4.3. The proportions of the two polymers, and hence the physical properties of a particular starch, depend upon its source. Regular corn contains about 26% amylose; waxy corn contains practically none; amylomaize contains up to 80% (Table 4.1).

The term "amylose" describes a mixture of essentially linear polymers, with chain lengths from a few hundred to a few thousand units (average molecular weight up to 600,000 or so). Amylose exists in the form of a relaxed helix which complexes with a number of materials, including iodine and fatty acids (Sections 4.3.3 and 4.3.5). The linear character of the chains facilitates hydrogen bonding, a loose association between hydroxyl groups on adjacent molecules, which, under appropriate conditions, gives rise to the phenomenon of "retrogradation", a form of crystalline precipitation (Section 4.4.4). This property is retained even after partial hydrolytic degradation of the molecule.

In contrast, amylopectin has an extremely large molecule of up to 1,500,000 anhydro-glucose units (molecular weight about 250,000,000). The structure is highly ramified with an average branch length of about 20 units. The branched structure inhibits hydrogen bonding so that amylopectin does not readily precipitate and, in concentrated solution, forms a soft stringy gel on cooling. Amylopectin solutions have an initially high viscosity but are readily degraded by continued agitation.

Where the properties of amylopectin are desired, for example as a base for many modified food starches, it is obtained almost in a pure form by milling waxy maize (Section 1.3.6). Likewise amylomaize (Section 1.3.7) provides starches very high in amylose. These starches are, of course, in granular form.

Some portion of amylose may be leached into solution by treating corn starch granules with warm water; also it may be selectively precipitated as a powder from well dispersed corn starch solutions. However, these are specialized operations, not part of normal wet milling.

4.3.2 Reducing properties

Neither amylose nor amylopectin as such possess any appreci-

able "reducing power". This property, possessed by glucose and fructose and a number of other sugars is exhibited by reaction with alkaline copper solutions, resulting in the precipitation of cuprous oxide.

The active group responsible for reducing power occurs at the 1-carbon position of the glucose molecule, and in a polymer chain all such groups except the end one are blocked by the 1-4 linkages between glucose units. The molecules are so large that the number of available reducing groups at the chain ends is not significant.

However, when the polymer chains are split by hydrolysis more reducing groups become available, and the degree of hydrolysis can be measured by this effect. Expressed as the percentage of glucose (dextrose) that would have the same reducing power, this is the Dextrose Equivalent (D.E.) of a hydrolyzate. Complete hydrolysis to dextrose, never achieved in practice, would result in a 100 D.E. product.

4.3.3 Iodine reactions

Ordinary corn starch in solution reacts with a solution of iodine in potassium iodide to give the characteristic brilliant blue color. Starch granules are also stained by iodine, but often so densely as to appear black.

The coloration is due to an inclusion complex formed between iodine and the amylose molecule, with iodine atoms occupying the center of the polysaccharide helix. The reaction is specific, and the amount of iodine bound under defined conditions may be used as an analytical measure of the amount of amylose present. Amylopectin does not bind any significant amount of iodine under the conditions used, and gives a red coloration, normally masked by the intense blue due to the presence of amylose. Waxy maize starch, which is predominately amylopectin, stains purple.

The helical configuration of amylose also is responsible for complexes with other materials, including lipids which are normally present in corn starch. For quantitative purposes the starch is de-fatted prior to being dissolved for measurement of iodine binding.

The iodine color with amylose varies with the degree of polymerization (DP). When the amylose chain length is reduced by acid or enzyme hydrolysis, the iodine color progresses through

purple, at a DP of 100 or so, to brown, at a DP around 20.

Temperature affects the blue starch iodine color, which disappears as the solution is warmed, possibly due to distortion of the polysaccharide helix, reappearing on cooling.

4.3.4. Optical rotation

Starch solution exhibit strong optical rotation, both amylose and amylopectin having a specific rotation (20°C, sodium D line) of +203°. This provides a convenient method of determining starch in many products, since interfering optically active material is readily washed out of the granular starch prior to gelatinization.

Acid or enzymic breakdown of starch to smaller saccharides can be readily followed by the decrease in optical rotation, the theoretical limit being reached at the specific rotation of dextrose.

4.3.5. Impurities

Commercial starches contain minor amounts of residual impurities, commonly proteinaceous and lipoid compounds.

A typical corn starch has an analysis as follows:

Carbohydrate	99.0% Dry basis
Protein (N x 6.25)	0.35% " "
Soluble Protein	0.010-0.015% "
Fat	0.55% " "
Ash	0.10% " "
Phosphorus (as P)	0.01 - 0.02% Dry basis
Moisture	12% Commercial basis

Note that in the wet milling industry "protein" is conventionally measured by multiplying the total Kjeldahl nitrogen content by 6.25. When applied to "soluble protein" this analysis largely represents polypeptides and amino acids.

Some of the protein derives from the matrix in which the starch granules were originally embedded in the corn kernel. The amount of protein present in finished starch may be greater or less depending on the care taken in manufacture, but, with corn starch, it is difficult to reduce this below about 0.25%. Some of this residual may be associated with fatty material and com-

plexed with amylose.

Very little fat can be extracted from starch by normal fat solvents (petroleum ether or carbon tetrachloride) unless the starch is first subjected to acid hydrolysis. However, most of it can be slowly removed from granular starch by extraction with a hydrophilic solvent such as methanol, containing a little water. The process can be speeded up by first ball-milling the starch.

The lipid material in corn starch is largely present in the amylose fraction and is associated with some phosphorus and nitrogen, although a larger amount of phosphorus is esterified to the starch itself.

Although present in fairly small amounts, such impurities can have a measurable effect on the properties of starches. For example the esterified phosphate in potato starch (0.05 - .10% as P) has a significant influence on the buffering power of hydrolyzates made from it, and de-fatting of corn starch reduces the gelatinization temperature by several degrees and reduces the peak viscosity.

4.3.6 Moisture

Starch in granular form is insoluble in cold water but establishes an equilibrium with moisture in the surrounding atmosphere (5). At room temperature and 50% relative humidity this corresponds to about 12% moisture, which is normally taken as typical. The adsorption phenomenon exhibits hysteresis, i.e. the exact moisture level depends on whether equilibrium is being approached from a moister or a drier state.

4.4 SOLUBILITY

4.4.1 Thermal gelatinization

When a suspension of starch in water is heated, the granules initially swell a little with adsorption of moisture, but retain their birefringence. If heating is continued, a point is reached at which, over a temperature range characteristic of the particular starch, the granules swell abruptly to many times their original size. This "gelatinization" is irreversible and is accompanied by the loss of optical properties, which provides a convenient means of following the change. It corresponds to the point at which the thermal energy is sufficient to overcome the

hydrogen bonding that stabilizes the granular structure.

The granules of a particular starch do not all gelatinize at the same temperature. The range for corn starch is approximately $62^{\circ} - 72^{\circ}\text{C}$ ($144-162^{\circ}\text{F}$), but smaller granules tend to be more resistant to gelatinization and occasionally may require heating to 100°C (212°F) or above. High amylose starches invariably require autoclaving above 100°C for complete gelatinization.

At the point of gelatinization the slurry becomes relatively translucent, and its viscosity increases markedly as the swollen granule aggregates interfere with each other.

As heating continues, particularly if the paste is agitated, some of the swollen granules are disrupted, and hydrated starch passes into colloidal solution, with an accompanying loss of viscosity. A significant degree of dispersion, such as is required for maximum accessibility to enzymic degradation, requires substantial mechanical shear (e.g. homogenizing), or superheating under pressure followed by flashing to atmosphere. Most starch pastes contain swollen granules and granule fragments as well as molecularly dispersed starch.

The gelatinizing temperature range of a particular starch varies somewhat with the conditions of test. The slurry pH can have an effect (Section 4.4.2), but in the range 5-7 it is not significant. The presence of certain chemicals, such as sodium nitrate and urea, lowers the gelatinization temperature, as does esterification and etherification of the starch itself. Other chemicals, typically sodium sulfate, act to increase the gelatinization temperature, presumably by competing for the available water.

Thermal gelatinization is an endothermic process, the "heat of swelling" depending somewhat on the extent of any starch granule damage. Recent measurements (6) indicate a typical value for corn starch of 4.3 cal/gram abs. dry starch (equivalent to 7.7 BTU/lb. dry substance).

4.4.2 Chemical gelatinization

A number of chemicals will disrupt hydrogen bonding and cause swelling and dissolution of starch granules at room temperature. The commonest of these is caustic soda; other reagents with this property include urea, dimethyl sulfoxide and salts such as salicylate, thiocyanate and iodide.

A caustic soda solution of starch is assumed to contain starch broken down to the molecular level (i.e. with no granule fragments), and this is commonly used to establish the "inherent viscosity" of starch. Solutions of starch in dimethyl sulfoxide are often used in the study of starch molecular structure and reactivity.

4.4.3 Acid degradation

In the manufacture of commercial corn syrups, corn starch is gelatinized and simultaneously hydrolyzed by the use of acid, usually hydrochloric acid, at high temperature under pressure. This results in a random hydrolytic splitting of the starch molecules with rapid loss of viscosity and progressive development of reducing sugars. For most purposes, only a partial hydrolysis is required, but in any case it is impracticable to achieve complete degradation because of side reactions which are favored at the high starch concentrations used, and which give rise to isomaltose, gentiobiose and other reversion products. For further details see Section 7.4.

4.4.4 Retrogradation

As described above, corn starch can be obtained in aqueous solution by thermal hydration and suitable dispersion. The solution so obtained is stable if kept above 90°C (194°F), but on cooling undergoes "retrogradation". In dilute solution below 70°C (158°F) this takes the form of an amorphous precipitation of part of the starch; in a solution of 5% or so, a hard gel is produced with further cooling. This phenomenon is largely attributable to the amylose fraction, the linear molecules reassociating by means of hydrogen bonds to give insoluble aggregates. Amylopectin by itself is reasonably stable in dilute solution, and in concentrated solution forms only a soft stringy gel on cooling.

The crystallization of amylose in this way provides a means of separating it from amylopectin. The precipitate is difficult to redissolve, even in boiling water, but dissolves readily in dilute alkali or dimethyl sulfoxide.

This type of retrogradation is inhibited by introducing groups such as acetyl or carboxyl into the starch molecule; presumably the substituent groups interfere with the orientation

of linear amylose which is required to facilitate hydrogen bonding. It is enhanced by a light degree of hydrolytic breakdown, so that acid converted syrups of low D.E. (under 30) are particularly prone to haze formation if allowed to cool during processing, or during storage of the finished syrup. This can be prevented by using bacterial amylase for "destarching", as described in Section 7.2.2.2. Acid-converted syrups are not very uniform in their composition, and the enzyme preferably attacks the larger molecules that tend to reassociate. Most acid-converted syrups above 30 D.E. and most enzyme-converted syrups above about 15 D.E. do not contain molecules of sufficient size to exhibit normal retrogradation.

A different phenomenon known as "high temperature retrogradation" (7) occurs when well-dispersed, very low D.E. starch solutions are kept at 75°-90°C (167°-194°F). Under these conditions, pastes prepared by autoclaving untreated starch at 150°C (302°F), or jet cooking starch with temperature-resistant amylase at 95°C (203°F), precipitate an amylose-fatty acid complex in the course of an hour or so. The precipitate takes the form of brittle "granules" 15-40 microns in diameter, which have some degree of crystallinity, exhibiting a polarization cross.

This material might be mistaken for native starch, but the granules are two to three times as large as those of unswollen starch, and have a more rounded appearance; also they are quite susceptible to mechanical damage, to give "pie-slice" fragments.

High temperature retrogradation is inhibited by esterifications (e.g. acetylation) of the starch and by etherification, but introduction of carboxyl groups by oxidation has no effect. Enzyme-liquefied starch loses this tendency to retrograde after a certain degree of hydrolysis, but the exact point is not well defined.

4.5 MODIFICATION

For many applications, both for food and for industrial use, it is advantageous to carry out minor chemical modifications to native starch. Most such modifications are carried out on granular starch in aqueous suspension prior to drying. The dried granular material is superficially similar to regular starch, but the physical characteristics of the cooked product are altered in some respects.

Modification can be carried out to reduce the hot viscosity of the paste, so that higher dry substance levels can be handled, to inhibit retrogradation, to stabilize the paste against mechanical shear or low pH, and so on. Further details are given in Chapter 10.

4.6 EVALUATION

Many routine procedures for chemical and physical analysis of native and modified starches are published by the Corn Refiners Association (8). A few points of particular interest are referred to here.

4.6.1 General properties

For the manufacturer of corn syrups, the important characteristics of starch, which is usually handled as slurry, are the total protein and the soluble protein content. A typical analysis for such a starch is given in Section 4.3.5.

When starch, or modified starch, is used for other purposes, normally as thickener or binder, the viscosity under standard conditions is of critical importance (Section 4.6.3), and total protein, pH, cleanliness, ash, and sulfur dioxide may also be relevant.

4.6.2 Simple Cook

A preliminary evaluation of the characteristics of an unknown starch may be made by a simple cook of a 5% slurry. A standard amount in a beaker is manually stirred with a glass rod while heating in a steam or boiling water bath.

Judgment can be made of the viscosity when hot, the extent of the "string" when the stirring rod is removed from the cook, and the texture and clarity of the paste while hot and on cooling.

Basic paste characteristics for different types of starches are given in Table 4.1, but when possible it is desirable to compare an unknown starch against a known one, cooked simultaneously. Simple modifications will affect the cook; for example an acid-thinned starch is thin when hot but sets up to a hard jelly on cooling, whereas an oxidized starch is thin both hot and cold (see Chapter 10 for further details).

4.6.3 Viscosity

The viscosity of a hot cooked starch paste is due in part to interference between swollen granules and in part to the inherent effect due to large molecules in colloidal solution. This means that the results obtained are very much dependent on the technique of cooking, particularly the amount of shear involved, and on the actual test procedure.

Measurement of "inherent viscosity" avoids the cooking problem by achieving essentially complete (molecular) dispersion with strong alkali (CRA procedure B-61). Even so, the large molecules imparting viscous properties are susceptible to breakdown on further agitation, and the measuring technique, using a U-tube viscometer, must be carefully standardized.

Variations of the "inherent viscosity" test (9) are in common use for control of starch modification processes where the molecular chains are being split by the use of acid or by oxidation. Such measurements are made by timing the flow through a calibrated funnel orifice, and are expressed as an "alkaline fluidity" on a scale where 0 corresponds approximately to unmodified starch and 100 corresponds to water.

The more functional "hot paste viscosity" is measured in many different ways, any one of which may give useful comparative results if the technique is sufficiently well standardized.

The "Scott" procedure has been widely used for regular and lightly modified starches. This technique employs mechanical stirring of a starch slurry in a metal beaker, using an insulated water bath maintained at boiling temperature by live steam. After cooking, the hot paste is placed in the "Scott cup" maintained at bath temperature, and the time for 100 mL to flow through the orifice is measured. The number of seconds taken is the "Scott viscosity"; regular starch falls in the range 70-120.

Much more comprehensive information on the properties of a starch is obtained by using the Brabender Viscoamylograph (10). In this instrument (Figure 4.4) the viscosity of a starch slurry is measured and recorded continuously as it is automatically cooked and subsequently cooled (CRA Method B-9). Agitation is provided by a number of fixed pins in the rotating sample cup, which work in conjunction with pins mounted on a sensor loaded by a torsion spring. A higher viscosity causes more drag, with a consequently greater deflection of the sensor, and this is re-

corded on a strip chart.

During the cooking cycle, the temperature is initially raised at 1.5°C per minute by a programmed thermoregulator which controls a heating jacket. At a suitable maximum, usually 95°C, the temperature is held for a few minutes with continued agitation. The thermoregulator is then put into reverse, and the sample is cooled.

The viscosity trace (Figure 4.5) achieved during a program of this sort provides an evaluation of the sample in several respects:

1. The point on the trace at which the viscosity increases abruptly gives a measure of gelatinization temperature. This basically depends upon the type of starch, but it is lowered by certain hydrophilic modifications, such as oxidation or acetylation, and by the presence of strong alkali or certain other chemicals. It is raised by cross-linking modification; in the presence of certain salts such as sodium sulfate and sodium chloride; and in the presence of a large amount of sucrose.
2. The peak viscosity shown on the trace is a measure of the "strength" of the starch. It can be adversely affected by poor processing conditions, for instance excessively long steeping, or by artificially drying the corn at too high a temperature, so that kernels exceed 140°F.
3. The extent to which the viscosity of the paste resists break-down on continued agitation at temperature indicates the stability that can be expected of the starch when in use. A starch such as waxy maize, which has a very high viscosity peak, tends to break down substantially; when cross-linked by modification the peak is reduced and the stability is improved.
4. The viscosity of a cold paste bears no particular relationship to the hot viscosity, but is indicative of the type of starch and any treatment it may have received in manufacture. For example, a light acid treatment of corn starch reduces its hot viscosity, but may actually increase the cold viscosity owing to a more pronounced tendency to retrograde.

It should be noted that if a starch actually forms a solid gel during test the results are not meaningful as the gel will fragment. It should be tested at a lower concentration.

FIGURE 4.4
BRABENDER VISCOAMYLOGRAPH

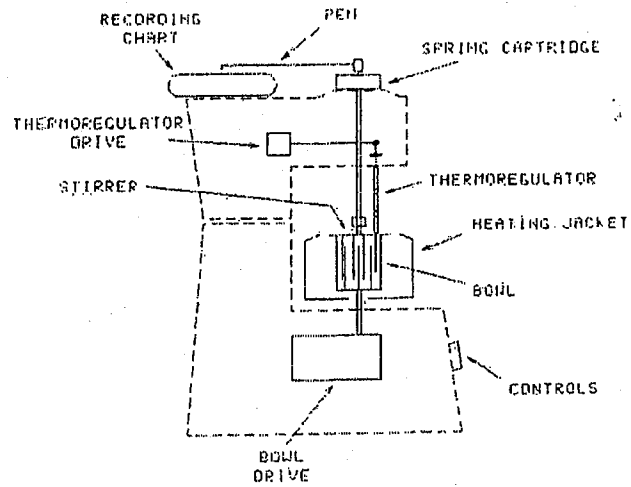
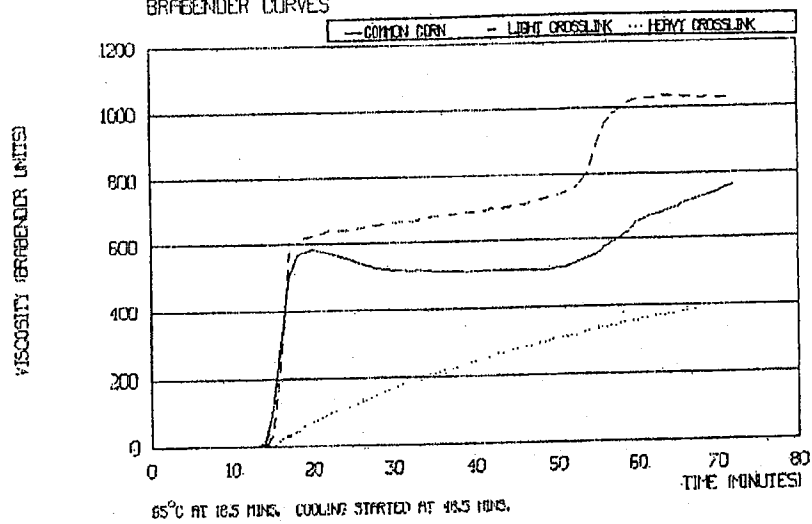


FIGURE 4.5
BRABENDER CURVES



4.7 MICROSCOPY

Routine microscopic examination of a starch may include its appearance in normal and polarized light, the gelatinization characteristics and the effect of staining with iodine or specific dyes (11).

This requires a microscope with magnifying power up to about 450X, with polarizing attachment (Nicol prisms), a calibrated eyepiece micrometer and a hot stage (Kofler or similar). A hemocytometer counting chamber is also of value for some observations.

4.7.1 Granule size and shape

The type of starch present in an unknown sample can often be determined from the appearance of its granules. Samples are conveniently studied in an aqueous suspension of about 0.2% and comparison made with the descriptions given in Table 4.1 and with genuine samples of known starches.

As shown in Figure 4.2, many corn starch granules are roughly round in shape, but there are also a number which are polygonal, resulting from areas of denser packing in the kernel. Granules are from 5-25 microns in diameter, the weight average being about 15. In many cases the hilum, or botanical point of origin of the granule, is visible as a small spot, and sometimes minute cracks can be seen radiating from this point.

Sometimes the factory drying process causes granules to clump together. Generally, these aggregates disperse in water, and, when this phenomenon is of particular interest, the starch should be slurried in glycerol for examination.

Glycerol may also be used as a mounting medium for pregelatinized starches, which swell and become very viscous in aqueous slurries. However, a satisfactory identification of the typical starch from which such material was made usually depends on finding a few ungelatinized granules. This is facilitated by thinning a warm aqueous sample suspension with liquefying amylase and examining the remaining sediment.

4.7.2 Effect of polarized light

As described in Section 4.2.2, most starch granules are birefringent and exhibit a polarization cross when examined in the dark field produced by partially cross Nicol prisms. This

characteristic is useful in identifying starch granules in mixture with other materials, but is of limited value for identification of the type.

4.7.3. Gelatinization temperature range

It was mentioned in Section 4.4.1 that, when starch is heated in aqueous suspension, the granules swell extensively and lose the polarization cross. Thus, a microscope equipped with a hot stage provides a sensitive means for determining gelatinization temperature.

As described by Watson (12), a prepared slide of a given starch sample is gradually heated ($2^{\circ}\text{C}/\text{min}$) while being observed under partially crossed Nicols. It will be seen that individual granules gelatinize quite sharply, but the temperature varies from granule to granule over a range which is characteristic of the particular starch species. $62^{\circ}\text{--}72^{\circ}\text{C}$ ($144^{\circ}\text{--}162^{\circ}\text{F}$) is typical for regular corn.

For accurate comparisons, the percentage of granules gelatinized at each temperature can be plotted, but for most purposes the temperature values at which 2%, 50% and 95% gelatinization takes place are sufficient.

The gelatinization temperature range is affected by modifications of the starch, or by incorporating salts or sugars into the cook. Table 4.3 gives a selection of values quoted by Schoch and Maywald (13). When a particular solute raises the gelatinization temperature, as for high levels of sucrose, it may be assumed to be competing for the available water. When it lowers it, as for sodium hydroxide, it appears that the reagent destroys the hydrogen bonds essential to the granular structure.

4.7.4 Staining

The most common "stain" used in starch work is iodine solution, which may be used to identify starch granules or fragments in admixtures with other materials and to distinguish blue-staining regular starch from the red-staining waxy type.

Iodine is often available as a 1% complex solution in 5% potassium iodide. A drop of such stain is placed in contact with the edge of an aqueous mount of the starch under a cover slip and is drawn into the sample by touching a piece of absorbent paper to the opposite edge of the cover slip. This technique presents

TABLE 4.3

GELATINIZATION TEMPERATURE OF VARIOUS STARCHES °C

Corn	62-72	Rice	61-78
Waxy maize	63-72	Grain sorghum	68-75
High amylose	67-100+	Waxy sorghum	67-74
Wheat	52-64	Sago	60-72
Potato	56-69	Tapioca	52-64
Sweet potato	58-74	Barley	51-60
Acid modified corn starch:	40 fluidity		62-72
	60 fluidity		63-73
	80 fluidity		68-77
Oxidized corn starch:	low conversion		55-73
	medium conversion		54-70
	high conversion		52-68
Cross-linked starches:	Corn		62-74
	Waxy maize		63-76
	Waxy sorghum		67-77
Cationic starch:	.046 degree of substitution		52-65
Hydroxyethyl sorghum starch:	.06 degree subs.		61-68
	.10 " "		58-67
Corn starch in sucrose solution, % :	5		61-72
	10		60-74
	20		65-78
	30		70-81
	40		72-85
	50		76-91
	60		84-97
Corn starch in NaOH solution, %	0.2		56-70
	0.3		49-65
Corn starch in Na ₂ CO ₃ solution, %	5		64-75
	10		67-76
	20		78-87
	30		92-103
Corn starch in NaCl solution, %	1.5		68-77
	3.0		70-79
	6.0		75-83
Corn starch, heat-moisture treated by refluxing in diacetone alcohol			68-76

a useful range of staining densities at the advancing boundary of the stain; it will be observed that heavy staining obscures the polarization cross of whole granules, and that partially swollen granules, which do not present a polarization cross, require a high concentration of stain to show significant color.

Routing testing of starch for "waxy or non-waxy" in a mixture (CRA procedure B-64) involves suspending the starch in a more dilute iodine solution (about .04%) and then counting the blue-staining and red-staining granules in a hemocytometer field.

Dyes may be used to establish the ionic character of unknown starches. For example, Methylene Blue, which is a positively charged (cationic) dye will stain anionic starches, which include oxidized starch, phosphate esters and potato starch (a natural phosphate ester). The washed starch is suspended in a 0.1% solution of the dye for a few minutes, washed free of excess dye and examined.

Likewise, cationic starches, prepared by the incorporation of substituted ammonia groups, are stained by negatively charged anionic dyes (e.g. Light Green SF Yellowish). In all such cases, it is helpful to compare an unknown starch with a known sample, tested in the same way.

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